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OXIDATION OF GALLIUM ARSENIDE IN A PLASMA  
MULTIPOLE DEVICE.

STUDY OF THE MOS STRUCTURES OBTAINED

Serge Gourrier, Andrei Mircea, Francois  
Simondet

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16. Abstract The oxygen plasma oxidation of GaAs was studied in order to obtain extremely high-frequency responses with MOS devices. In the multipole system (magnetic confinement associated with a hot cathode), a homogeneous oxygen plasma of high density $5 \times 10$ to the $10$ power/cm cm) can easily be obtained in a large volume. This system is thus highly convenient for the study of plasma oxidation of GaAs. The electrical properties of the MOS diodes obtained in this way are controlled by inter- face states, located mostly in the upper half of the band gap where densities in the $10$ to the $13$ power/sq cm x eV range can be estimated. Despite these interface states the possibility of fabricating MOSFET transistors working mostly in the depletion mode for a higher frequency cut-off still exists.		
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OXIDATION OF GALLIUM ARSENIDE IN A PLASMA  
MULTIPOLE DEVICE  
STUDY OF THE MOS STRUCTURE OBTAINED

Conclusions

/111\*

Work planned: Physics-Electronics

Grantee - Organization and laboratory: Contract No. 77-7-1638

Laboratoires d'Electronique et de Starting Date: 11/14/77

Physique Appliquee

3, avenue Descartes

94450 Limeil-Brevannes

Scientific Director:

A. Mircea, assisted by S. Gourrier

Duration: 12 months

Telephone: (1) 569-96-10

Cost: 352,000 F.

Number of investigators involved: 3

Subject of contract:

Study of insulating layers on GaAs and of their interfaces,  
with the view of using them for passivation and for fabrication  
of MIS transistors.

Original Objectives:

Formation of an insulating layer, mainly oxide, on the sur-  
face of GaAs by using plasma techniques.

Study of metal-insulator-semiconductor structures so obtained.

Have these objectives been attained?

Yes, for oxide on GaAs used as an insulator.

Manufacture of depletion and enrichment MOSFET transistors  
can be anticipated.

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\*Numbers in margins indicate foreign pagination.

Have objectives other than those originally intended been achieved?

Construction and perfection of a multipole plasma source suitable for plasma oxidation of GaAs.

Do you see any objection to dissemination of the final report?  
No.

Have any scientific publications already reported your work? /iv  
Yes.

Have any patents come out of this research?  
No.

Can and should the contract have a continuation?  
Yes, pursuit of the research plan.

Would you wish to receive a possible DGRST contract for exploitation of the results obtained?  
A contract will be requested later to extend this work.

General conclusion about the investigation:  
We have developed a plasma source well suited to the problem of oxidizing GaAs.

The results obtained so far are encouraging.

Scientific Publications

Work planned: Physics-Electronics

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Contract number: 77-7-1638

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Laboratoires d'Electronique et de Physique Appliquee

3, avenue Descartes, 94450 Limeil-Brevannes

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Study of insulating layers on GaAs and of their interfaces,  
with the view of using them for passivation and for fabrication  
of MIS transistors.

- S. Gourrier, A. Mercea, M. Bacal

"Use of Multipole Plasma for the Oxidation of Semiconductors"

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3 Avenue Descartes, 94450 Limeil-Brevannes

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and

Study of insulating layers on GaAs/of their interfaces,  
with the view of using them for passivation and for fabrication  
of MIS transistors.

Nothing.



Various techniques have been used over the last few years to deposit or form an insulating layer on the surface of gallium arsenide. These studies have been performed to produce MOSFET field-effect transistors similar to the silicon devices. Use of gallium arsenide, in which the volume mobility and saturation velocity of the electrons are higher than they are in silicon, ought to lead to improved properties of MOSFET devices.

Various groups have already announced fabrication of such transistors on gallium arsenide, operating mainly by enrichment or depletion. For example, encouraging results have recently been obtained by a Japanese group at the Fujitsu laboratories, working on the oxidation of GaAs by oxygen plasma [1]. With a  $2\mu\text{m}$  gate length, an enrichment MOSFET has shown a maximum oscillation frequency of 13 GHz. For a depletion MOSFET with a gate  $1.8\mu\text{m}$  long, this frequency is about 22 GHz, 10% higher than that for an equivalent MESFET transistor (with Schottky gate) and of the same dimensions, made with the same technology but without oxidation). The depletion MOSFET produced 0.4 W at 6.5 GHz [2].

Such a promising result shows the value of this study.

The problem can be looked at in two ways;

- deposition of a "foreign" insulator on the semiconductor;
- transforming the material itself into an insulator, which up to now has meant oxidizing it.

In general, it appears that the main difficulties encountered in oxidation of GaAs are related to the differences in the physical-chemical properties of arsenic, gallium, and their compounds (heats of formation of the oxides, partial pressures).

In particular, the oxides of arsenic are distinctly more volatile than those of gallium:  $\text{As}_2\text{O}_3$  has a partial pressure of  $\angle 4$  1 atm at  $350^\circ\text{C}$ , while  $\text{Ga}_2\text{O}_3$  is virtually undecomposed up to  $2000^\circ\text{C}$ . As a result, there are differences in arsenic-gallium stoichiometry in the oxide (generally arsenic-deficient) and at the oxide/semiconductor interface (generally gallium-deficient and containing unoxidized arsenic). These differences in stoichiometry could be related to the poorer electrical properties of gallium arsenide MOS structures, compared to those on silicon. They also very probably explain the poor results obtained with "ordinary" thermal oxidation (without adding arsenic). In particular, absence or low levels of arsenic in the oxide greatly decreases the resistivity and the breakdown field.

Anodic oxidation of GaAs in an electrolytic bath is a simple technique to use, and has been studied very much lately [3], [4], but the oxides obtained this way contain OH radicals (if the electrolyte is based on water, which is the most frequent case) and some impurities from the bath.

Since the very encouraging results mentioned above [1], [2] and those of R.P.H. Chang [5], at Bell Laboratories [6], oxygen-plasma oxidation of GaAs seems the most interesting technique. This is a "dry" technology which can easily be integrated into a cycle for fabricating components without exposure to air. In addition, it is possible to work under high-purity conditions (ultra-vacuum) this way. It is also a more flexible technique: for example, by changing the plasma density the experimental conditions (oxidation time) and the properties of the oxides obtained can be modified. This is the technique chosen at LEP.

## II. Plasma Oxidation of GaAs

### II.1. - Principle

The general principle of the method is the following: an  $\angle 5$

Oxygen plasma is created by various techniques. The sample to be oxidized is placed in the plasma, and is generally biased positive with respect to the plasma. A bias current then passes through it. This is plasma anodic oxidation (there are, however, some cases in which the sample is electrically insulated).

In first approximation, this is an electrochemical anodic oxidation in which the electrolyte has been replaced by an oxygen plasma. But there are significant differences between the two techniques, one of which is due to the high electron component of the current received at the sample surface during plasma oxidation (cf. II.4).

We are now going to look briefly at the various techniques for generating an oxygen plasma, and at their application to oxidation of gallium arsenide, and then present the technique used at LEP and the properties of the oxides obtained.

## II.2. Various techniques for plasma oxidation of GaAs

Table 1 lists the main experiments on plasma oxidation of GaAs up to the present time.

The techniques most commonly used today for generating plasmas on the cold-cathode DC discharge [8] and the RF discharge, either with a coil [1], [9], [10] or between two plates [5]: The first is easy to use and gives plasmas of large volume but low density\* (a few times  $10^9 \text{ cm}^{-3}$ ) which have low oxidation rates. The second technique is harder to set up and to control, and gives plasmas of smaller volume but higher density (up to  $10^{12} \text{ cm}^{-3}$ ). The LAMP (large-capacity multipurpose plasma reactor) built on this principle at Bell

\* A plasma is neutral overall. The density of positive ions is equal to the total density of negative species (negative ions and electrons); this is the plasma density.

TABLE 1.

Type of Plasma	Authors	Properties of the plasma	Oxidation rate	Structure and composition of the oxide	Electrical properties
Microwave (2.5 GHz, 1 kW)	O. A. Weinrich (1966) [7]	High density ( $10^{13} \text{ cm}^{-3}$ )	$X^2 = kt$ 1000 Å in 10 min.	Amorphous	Not published
D.C. Discharge Cold cathode	L.A. Chesser, G.Y. Robinson (1978) [8]	Low density ( $10^9 \text{ cm}^{-3}$ )	Slow: 1000 Å/hr. Oxidation constant: $37 \frac{\text{Å}}{\text{V}}$	Deficient As-Interface (500 Å for 1800 Å of oxide)	$p \sim 10^{14} \text{ cm}^{-3}$ c(v) p max and min well defined n no inversion - frequency.
R.F. Discharge	T. Sugano, Y. Mori (1974) [9]		Very fast: 500 Å/sec (no bias)	general polycrystalline As-deficient	Not published
	K. Yamasaki, T. Sugano (1977) [10]		1000 Å/mm (with bias) 40 Å/V		$p \sim 10^{12} - 10^{14} \text{ cm}^{-3}$ $E_c \sim 10^6 \text{ V/cm}$ Frequency dispersion No inversion
	N. Yokoyama (1978) [11]	Magnetic confinement	Varies with confinement 500 Å/mm (no bias)	Amorphous	C(V) similar to Chesser - Robinson depletion, enrichment MOSFET $F_{\text{max}} \text{ depl.} = 13 \text{ GHz}$ $F_{\text{max}} \text{ enrich.} = 22 \text{ GHz}$ 2.4 W at 6.5 GHz $L = 1.8 \mu\text{m}$ Annealed 450 °C, $H_2$ C(V) $N_{\text{ss}}$ a few $\times 10^{11} \text{ cm}^{-2}$ Deep depletion n.
Hot Cathode Multipole	R. P. H. Chang (since 1976) [5]	Magnetic confinement $10^{10} \text{ cm}^{-3}$ $T_e = 4 \text{ eV}$ $T_i = 0, \text{ leV}$	500 Å/mm Saturates for $V_{\text{bias}} = \text{const.}$ Interface < 70 Å	Amorphous As-deficient Interface ~ 100 Å	C(V) p max and min quite sharp $Q_B \sim 10^{12} \text{ cm}^{-2}$ $N_{\text{ss}}$ a few $\times 10^{11} \text{ cm}^{-3}$ n frequency dispersion Deep depletion
	L.E.P. (1978)	Magnetic confinement $5 \times 10^9 - 5 \times 10^{10} \text{ cm}^{-3}$ $T_e \sim \text{leV}$	250 Å/mm saturates for $V_{\text{bias}} = \text{const.}$ 240 Å/V	Amorphous As-deficient Interface ~ 100 Å	

$Q_B$  charges held in the oxide ( $\text{cm}^{-2} \text{ eV}^{-1}$ );  $E_c$  Breakdown field;  $T_e$  Electron temperature;  
 $N_{\text{ss}}$  Density of interface states ( $\text{cm}^{-2} \text{ eV}^{-1}$ );  $C$  Resistivity;  $T_i$  Ion temperature

Labs by R.P.H. Chang [5] has given the most encouraging results up to now. It uses magnetic confinement of the plasma and allows decoupling of the plasma-generating region from the sample region. [7] This is at present one of the most complete and well-developed systems, allowing study and application of many plasma-state chemical reactions.

### II.3. The multipole system used at LEP

#### II.3.1. - Description

The device consists mainly of a hot cathode (filament) combined with a magnetic containment system (Figure 1). A hot filament biased a few tens of volts negative with respect to ground emits electrons. These are confined by an arrangement of vertical columns of permanent magnets placed facing the plasma alternately. Such an arrangement forms a "magnetic mirror" which reflects the primary electrons from the filament. This confinement can be completed by two plates at the top and bottom of the device, which also have permanent magnets arranged in the same way.

The whole thing (magnets + filament) constitutes a multipole, a device which has been studied in plasma physics for years [11], [12], [13], [14]. It offers many advantages: a) Electron confinement increases the mean free path of the electrons and thus their probability of ionizing an oxygen atom. The multipole thus allows the plasma density to be increased by one or two orders of magnitude, especially at relatively low gas pressures ( $10^{-4}$  to  $10^{-3}$  Torr). Consequently, in the multipole built at LEP, densities ranging up to  $5 \times 10^{10} \text{ cm}^{-3}$  have been attained with oxygen pressures of  $5 \times 10^{-4}$  to  $10^{-3}$  Torr. Figure 2 shows plasma density at  $6 \times 10^{-4}$  Torr as a function of filament emission current (primary electron current)  $I_{em}$  and of discharge power  $P_d$  (product of emission current and filament bias voltage). The plasma density varies approximately as  $I_{em}^{0.8}$ . It has been possible to obtain higher densities (in the range of  $10^{11} \text{ cm}^{-3}$ ) by technical improvements which allowed a higher filament emission current.

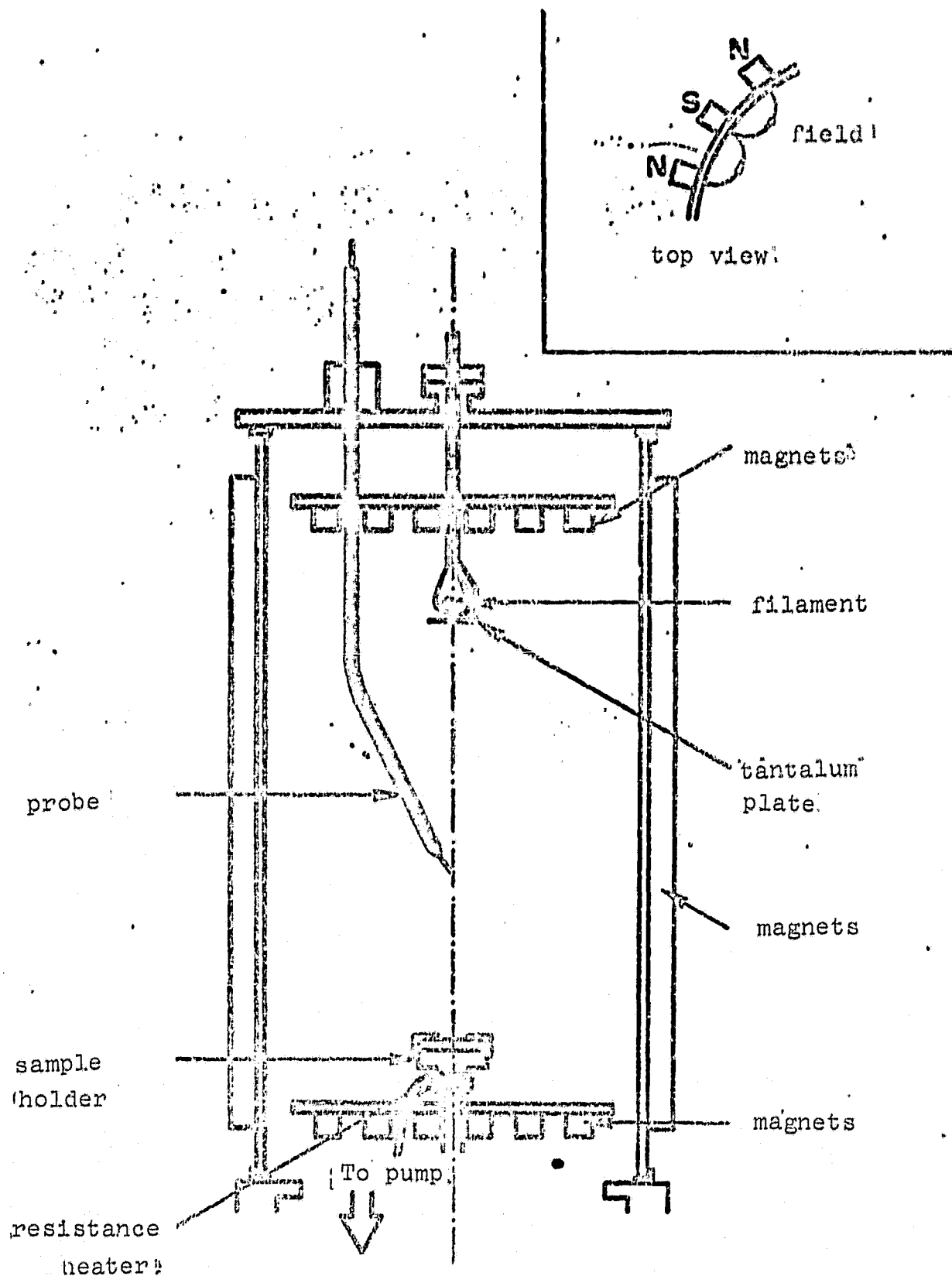


Figure 1. Diagram of the multipole  
(The insert shows a partial top view)

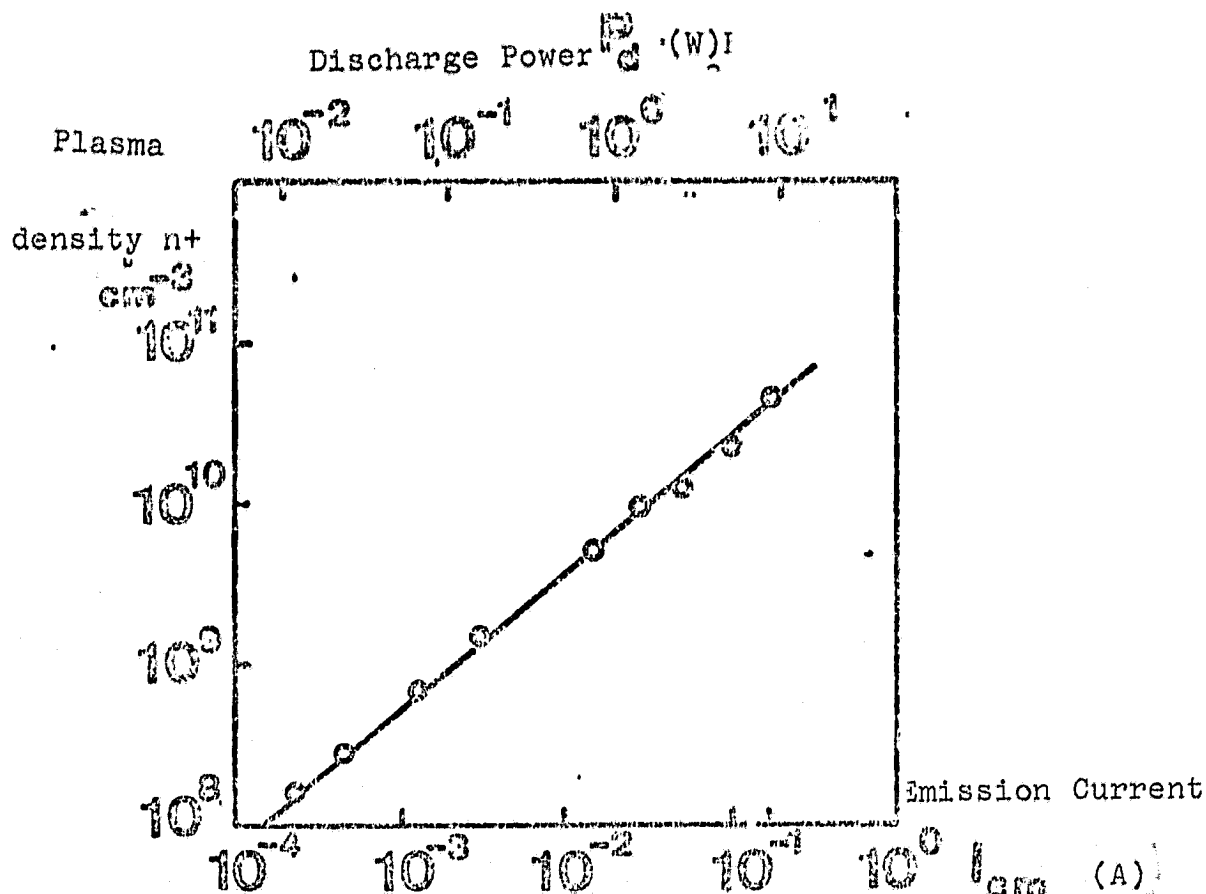


Figure 2. Plasma density  $n^+$  in the multipole as a function of emission current  $I_{em}$  and discharge power  $P_d$ .

b) - The electrons confined and re-injected into the plasma give good plasma uniformity, which is an essential condition for satisfactory uniformity of the oxidation. This uniformity can also be obtained in larger multipoles than the present one (15 cm diameter, 30 cm high), as work with the "PARODIE" multipole at Ecole Polytechnique (1 m diameter, 1 m high) has shown [14]:  $0.3 \text{ m}^3$  plasma can be generated in it, uniform to 1%. One can thus talk about construction of large multipoles for simultaneous oxidation of several wafers.

c) The low voltages needed to operate the multipole (a few tens of volts) limit sputtering from the cathode, which can be an important effect in other types of plasma, especially in the cold-cathode DC discharge [15].

In addition (this is a general property of the oxygen plasma),

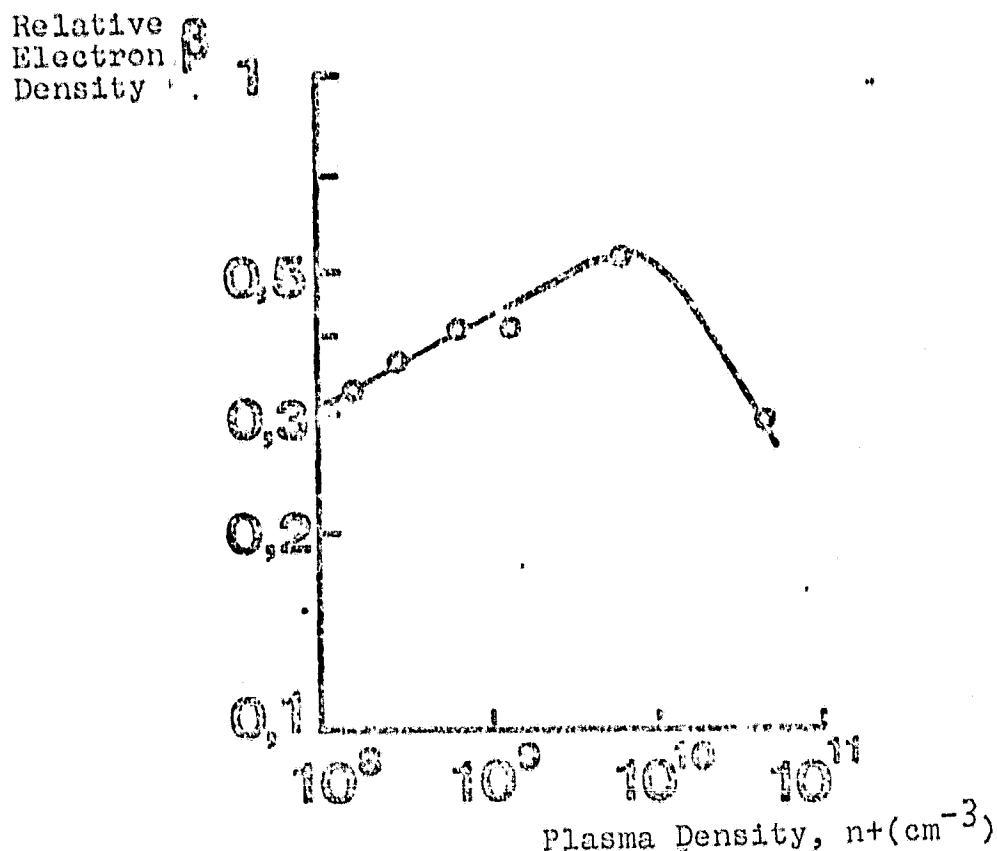


Figure 3. Relative electron density  $\beta$  in the multipole (as a function of plasma density)

there is a high proportion of negative ions in the multipole plasma. Figure 3 shows  $\beta$ , the ratio of electron density to total plasma density, as a function of plasma density. For a plasma ranging from  $10^8 \text{ cm}^{-3}$  to  $5 \times 10^{10} \text{ cm}^{-3}$ , the proportion of negative ions lies between 30 and 50% of the negative species. This is an interesting characteristic of the plasma, but it is not necessarily an advantage in the plasma oxidation of GaAs, because in this case it appears that the electron contribution to the current is essential (cf. II.4).

Estimates of the electron temperature give a value around 1 eV.

All the results mentioned above were obtained by interpreting the current-voltage characteristics of a Langmuir probe.



The calculations are discussed briefly in Appendix 1.

Mass analysis of the ionic species in the plasma has not been performed as yet. However, an analysis of negative ions in a similar plasma generated by a biased filament without magnetic confinement has shown that the dominant ionic species depends on the nature of the filament [16]: with a tungsten filament, the dominant negative ion is  $\text{NO}_2^-$  (the nitrogen coming from the residual gases); with a rhenium filament it is  $\text{O}_3^-$ . We have assumed that it would be the same in the multipole, especially for calculating the plasma density and the proportion of negative ions.

The sample holder (Figure 1) is a copper disc mounted on a copper support which is in contact with a block through which liquid nitrogen can be circulated. The sample holder disc is electrically insulated from the support (at ground) by a thin mica sheet.

A temperature regulator is mounted on the sample holder. At present, the temperature read by a thermocouple placed on the sample holder disc doesn't go above  $100^\circ\text{C}$  during a typical oxidation.

A tantalum plate below the filament prevents any sample contamination by line-of-sight evaporation.

A liquid-nitrogen cold trap is mounted under the sample holder.

### II.3.2. Oxidation of GaAs in the multipole

The system is pumped to about  $10^{-6}$  Torr by a diffusion pump, then back-filled with oxygen to between  $5 \times 10^{-4}$  and  $10^{-3}$  Torr.

Oxide Thickness

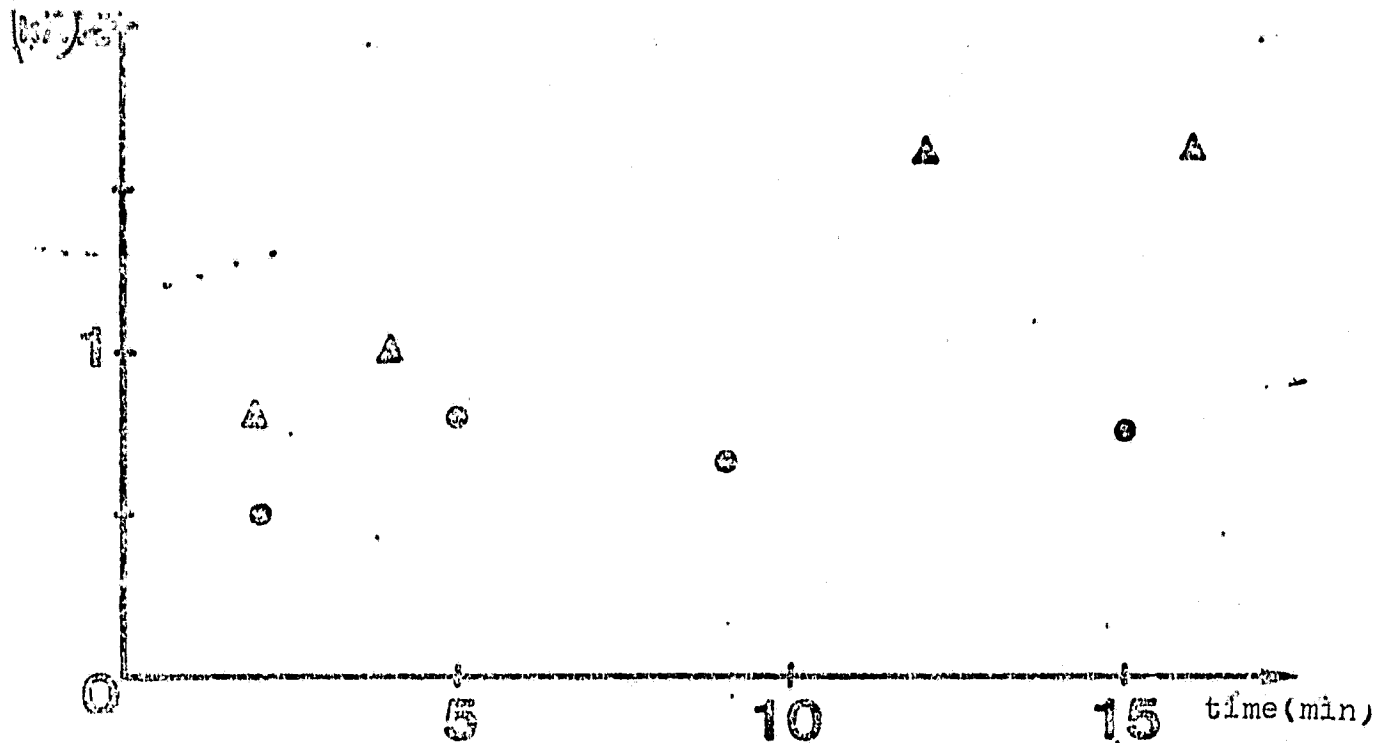


Figure 4. Oxide thickness as a function of time at constant bias voltage.

Bias Current Density, ( $mA cm^{-2}$ )

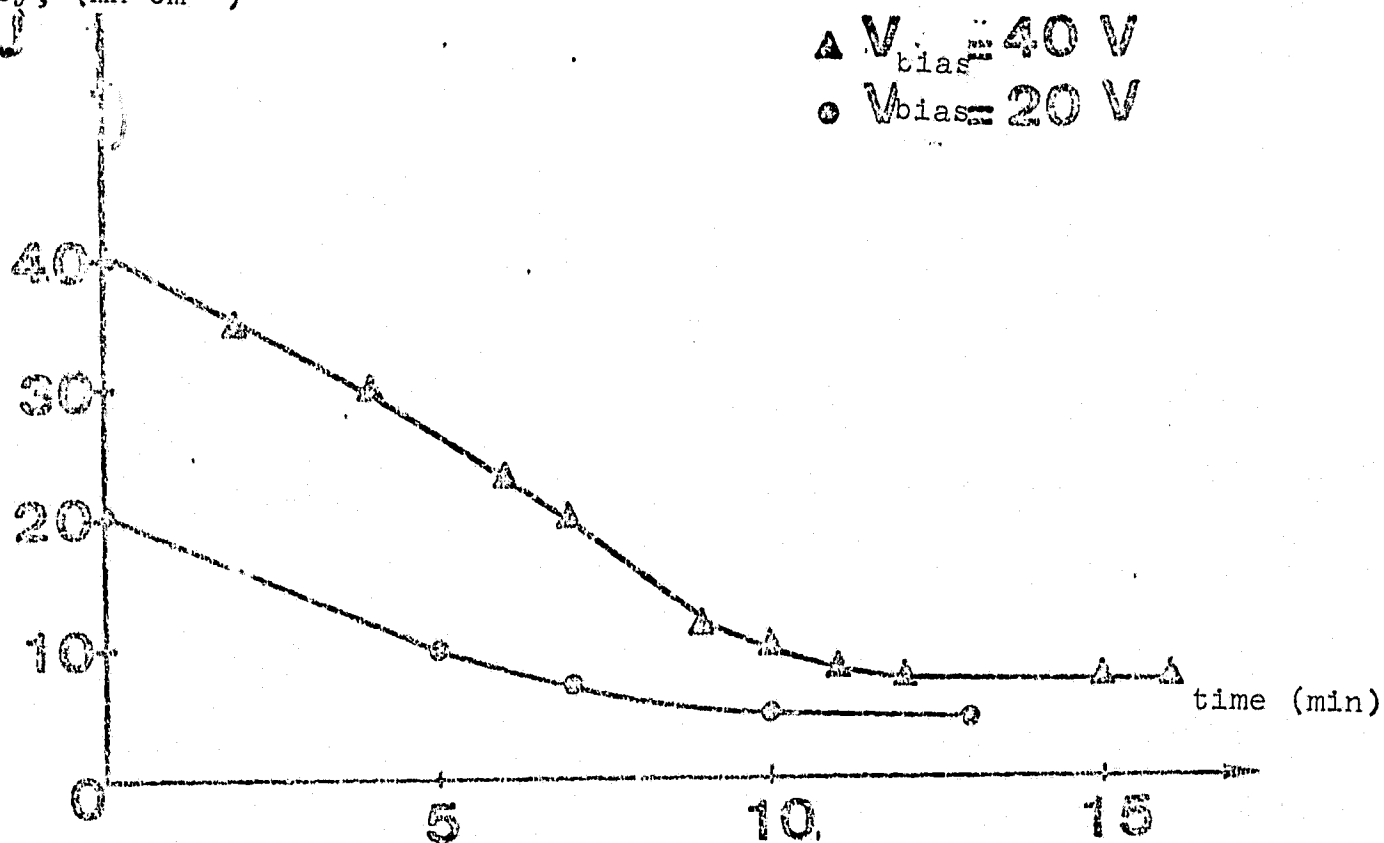


Figure 5. Bias current density as a function of time at constant bias voltage.

a) constant bias current

The growth rate is approximately constant when the bias voltage is not greater than 20-30V. For example, at a plasma density of  $2 \times 10^{10} \text{ cm}^{-3}$  growth rates of 200 Å/min and 250 Å/min can be obtained for bias current densities of 30 and 40 mA/cm<sup>2</sup> respectively.

The ratio of final thickness to change in bias voltage is about 40 Å/V, which confirms the results of other groups working on plasma oxidation of GaAs [5], [8]. This ratio is nearly half as large (22 Å/V) for electrolytic anodic oxidation [3], [4]. The origin of such a difference is still unknown.

The decrease in growth rate observed at high bias voltages (above 20-30V) is probably due to partial sputtering of the oxide layer by oxygen ions which have become too energetic. An estimate of the sputtering rate shows that it can be of the same order of magnitude as the growth rate (several Å/sec). This phenomenon, observed elsewhere [8], is one of the differences from electrolytic anodic oxidation. In the latter case, if one works at constant current the polarization voltage generally increases linearly with time.

b) constant bias voltage

/10

The oxide thickness is observed to saturate after a few minutes (Figure 4). A thickness of about 1000 Å is reached in 4 min at a bias of 40 V and a density of  $2 \times 10^{10} \text{ cm}^{-3}$ .

If the bias voltage is held constant, the bias current decreases with time but does not completely go to zero (Figure 5). This residual current (about 20% of the initial current) has also been observed by others [8]. Its origin has not been established clearly: it could be a photocurrent due to plasma radiation [8], a leakage current through the edges of the oxidized

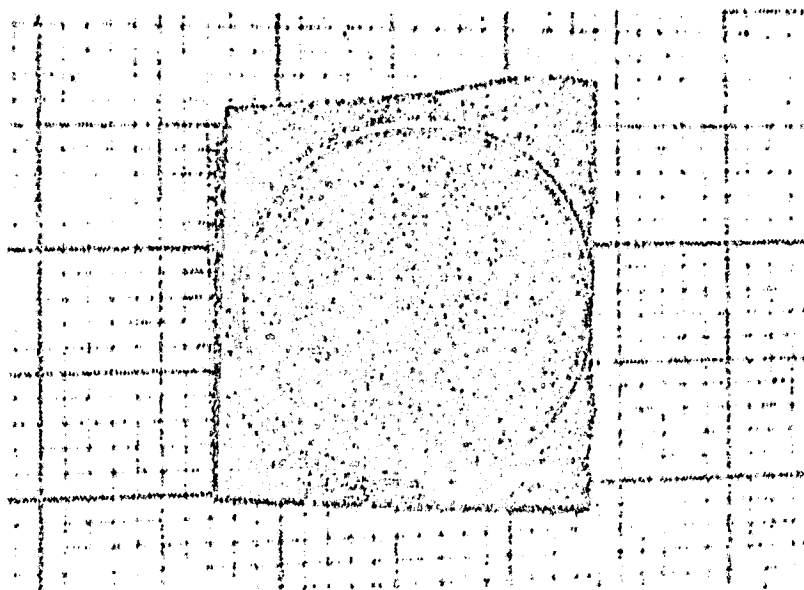


Figure 6. Photograph of an oxide (scale in centimeters)

area, which would be imperfectly screened by the aluminum mask, or a result of the sputtering noted above. In the latter case, the limiting oxide thickness would be reached when the sputtering rate is equal to the growth rate. This limiting thickness is less than the theoretical thickness limit, toward which it ought to tend if there were no sputtering, and for which the bias current would tend to zero. The residual current would then be the current corresponding to the limiting thickness really obtained.

We have not carried out any systematic studies of the effect of plasma density.

In summary, by one technique or the other, uniform oxides are obtained easily on a surface of up to  $2 \text{ cm}^2$  (Figure 6). This limit is presently imposed by technical considerations, but the good uniformity of the plasma in the multipole (see above) allows us to expect oxidation of larger surfaces or of several samples at a time.

Oxidations have been made with various types of sample, all with (100) orientation: n-type, with doping of a few times  $10^{16} \text{ cm}^{-3}$  to  $2 \times 10^{18} \text{ cm}^{-3}$  epitaxied on  $n^+$ , and p-type doped at  $7 \times 10^{15} \text{ cm}^{-3}$  epitaxied on  $p^+$ . The epitaxies were made at LEP.

#### II.4. = Comments on mechanisms of plasma growth of oxide on GaAs

/11

The mechanisms of plasma oxidation of GaAs are still poorly understood. They may vary with the type of plasma.

Oxide growth in a microwave plasma (O.A. Weinreich [7], Table 1) has been interpreted as implantation of oxygen ions in a layer about  $10 \text{ \AA}$  thick, followed by diffusion under the influence of the field. In this way, the observed parabolic dependence of thickness on time ( $x^2 = kt$ ) can be explained. In such a mechanism, only oxygen would be mobile.

For other types of plasma, and especially for the multipole plasma, it appears that the mechanism is inward diffusion of oxygen ions combined with outward diffusion of arsenic and gallium. This conclusion follows from oxidation experiments with Al/GaAs composite structures performed at LEP and at Bell Labs. After oxidation of such devices, gallium arsenide is found on both sides of aluminum layer, which is itself oxidized [6], [17]. Figure 7a shows an Auger profile (cf. III.1). of an oxidized Al/GaAs sample. Such a result shows that there is good backward movement of oxygen on the one hand, and of arsenic and gallium on the other.

In addition, the oxygen ions responsible for the oxidation could be extracted as such from the plasma, or even be formed at the GaAs surface - for example by interaction between electrons and oxygen molecules. To try to clarify this point, we have performed the following experiment: we placed permanent magnets /12

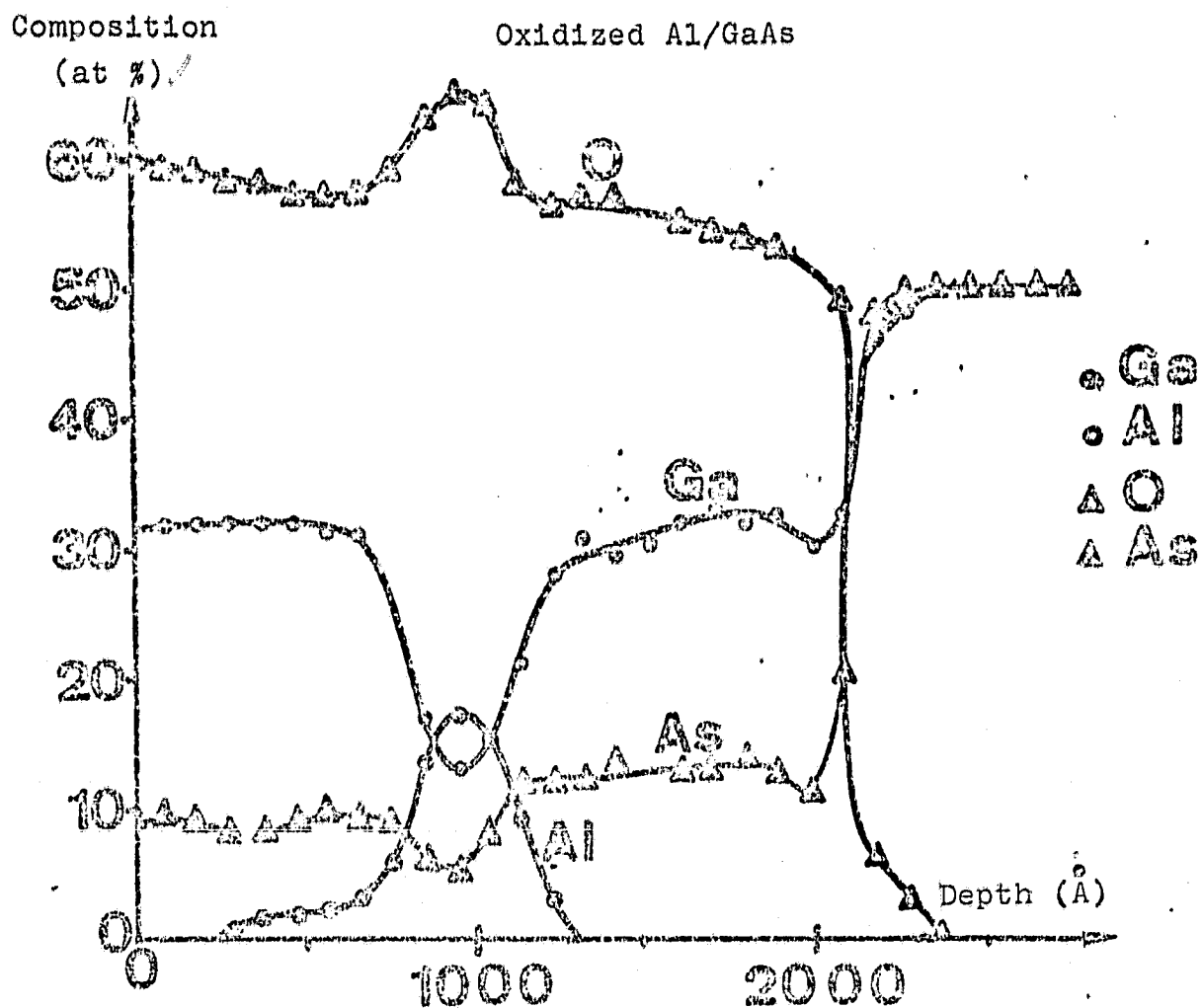


Figure 7a. Auger profile of an oxidized Al/GaAs structure.

near the sample so that the magnetic field (several hundred G) was parallel to the surface of the sample. A large drop in bias current was seen. For example, with a plasma density of  $2 \times 10^{10} \text{ cm}^{-3}$  and a bias voltage of +40 V, the bias current density dropped from  $40 \text{ mA/cm}^2$  to about  $1 \text{ mA/cm}^2$ . The magnetic field deflects the electrons near the sample and the electron component of the bias current is suppressed or greatly reduced. On the other hand, the ions are heavier, and virtually unaffected by the field. A very significant decrease in oxidation rate is thus seen. This simple experiment shows clearly that the electron component of the bias currents plays a fundamental role in the oxidation mechanism, and that the oxygen ions responsible for the oxidation are - at least for the most part - formed at the sample surface and not extracted as such from the plasma. This experi-

ment also shows the relative importance of the ion and electron components of the bias current. The electron component is undoubtedly the most important by far because of the higher mobility of electrons. R.P.H. Chang arrived at the same conclusion after a similar experiment [5].

Note: The special case of oxidation by a cold-cathode DC discharge has been studied in detail by Leslie, Keith, and Knorr [15], who oxidized various materials (Ta, Nb, Cu) by this method, using various cathodes (Ta, Nb, Al, C), and analyzed the oxide obtained by Auger spectroscopy. Their conclusion was that transfer of material from the cathode to the anode is not an interfering effect, but takes part in the oxidation process. The oxide would be formed in two stages: first, deposit of a layer of oxidized cathode material onto the surface of the sample, then exchange of oxygen between this oxide layer and the sample. If the oxide of the cathode material is chemically more stable than that of the sample, the latter does not oxidize (as with the carbon cathode).

Auger analysis of GaAs oxide obtained in a DC oxygen plasma with an aluminum cathode [8] has revealed a layer of aluminum oxide on the surface. Similar results have been obtained at LEP during preliminary tests of oxidation with a molybdenum cathode. Because of the low voltages used, such a phenomenon should not occur in the multipole, and in fact no contamination could be detected by Auger or SIMS (see below). /13

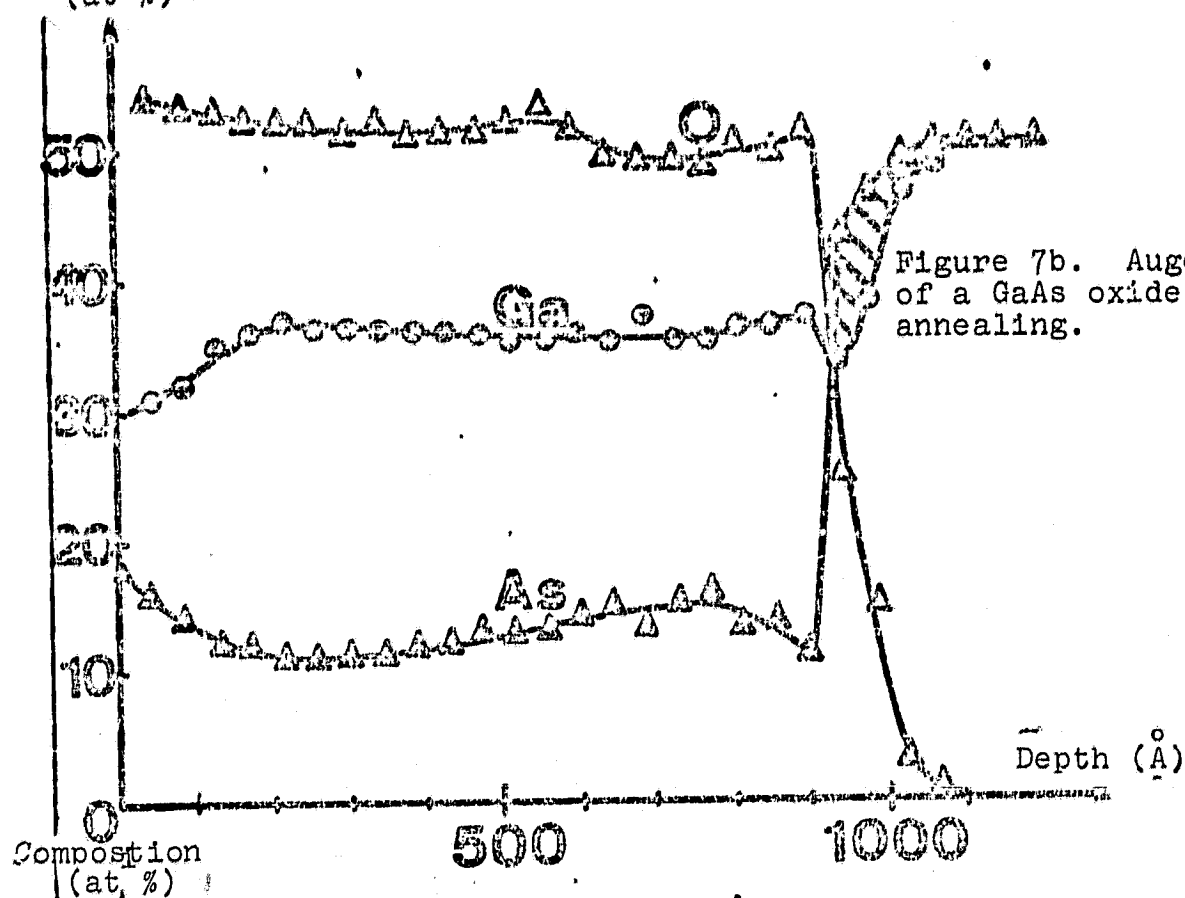
### III - Properties of Oxides Obtained in the Multipole Plasma

#### III.1. Physical-chemical properties

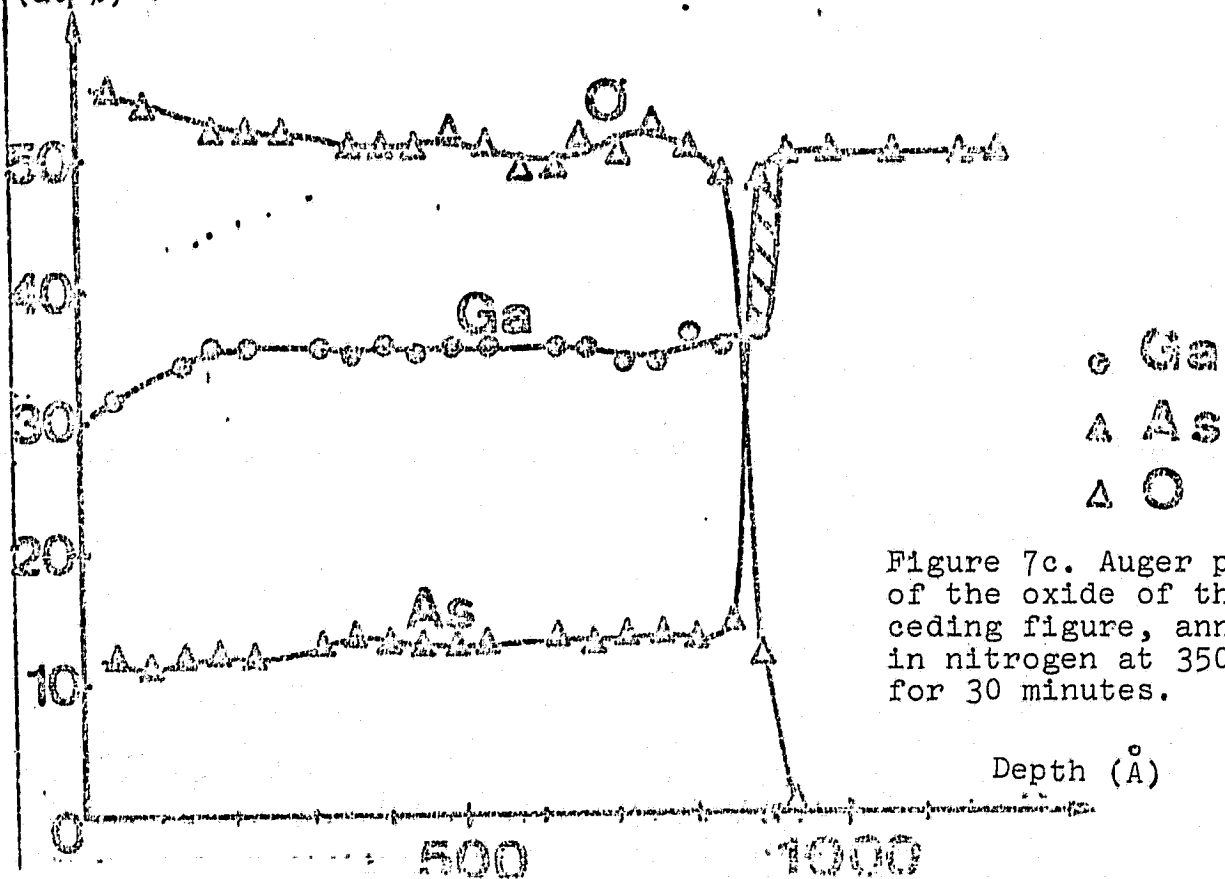
##### III.1.1. - Chemical properties

Like the electrochemical anodic oxide [3], [4], plasma-

Composition  
(at %)



Composition  
(at %)





produced oxide on GaAs is chemically delicate. It is attacked by acids ( $\text{HCl}$ ,  $\text{H}_3\text{PO}_4$ , etc.) and common bases; we have not yet carried out systematic quantitative (attack rate) studies on this subject however.

### III.1.2. - Physical properties

#### a) - structure

X-ray diffraction shows that the oxides are amorphous.

#### b) - optical properties

The index of refraction of the oxides, determined by ellipsometry at 632.8 Å is 1.85 - 1.9, comparable to results published elsewhere [1], [18].

#### c) - composition

The composition of the GaAs oxides produced in the multipole has been studied at LEP by SIMS and Auger spectroscopy in an ion-sputtering system.

SIMS has better detection limits than Auger spectroscopy. It was used to check that no contamination was present in the oxide. However, because of the difficulty of interpreting and quantitating SIMS spectra, we made most of the oxide-composition studies by Auger spectroscopy with ion milling. This technique is less sensitive, but the results can be made quantitative by use of calibration standards. The quantitation technique is detailed in Appendix 2.

The Auger spectrometer, made by CMA, was used with a 10- $\mu\text{A}$  beam current at 2.5 kV, and 5-V modulation. Ion etching was carried out at a beam density of about 6  $\mu\text{A}/\text{cm}^2$ , which gave an etch rate of 8 - 10 Å/min.

Figures 7b and 7c show typical Auger profiles of an oxide before (7b) and after (7c) annealing in nitrogen at 350°C for 30 min.

For the unannealed oxide one observes:

a) a practically flat profile over most of the volume of the oxide, with typical concentrations (in atom percent, a/o):  
O - 50 a/o; Ga - 35 a/o; As - 15 a/o.

b) an increase in the arsenic concentration and a decrease in the gallium concentration in a surface region about 200 Å thick.

c) an oxide-semiconductor interface containing an excess of arsenic (hatched region). The width of the interface can be estimated at about 100 Å if the distance over which the oxygen concentration goes from 90% to 10% of its maximum value is taken as an indication.

By comparison, for the annealed oxide the concentration in the volume is almost unchanged. However, the increase in arsenic in the surface region has disappeared: some of the arsenic escaped during annealing. The interface has been reduced to about 50 Å, and still contains an excess of arsenic. Finally, the thickness of the oxide seems to have decreased (but this change is small, and could be due to a lack of uniformity of the oxide).

The overall arsenic deficiency is probably explained by the volatility of the arsenic oxides, much higher than that of the gallium oxides.

/15

The deficiency of arsenic in the volume and the excess of arsenic at the interface have been observed in other oxides made by plasma [8], [19]. However, the width of the interface seems to depend on the experimental conditions, mainly on the length of the oxidation. For R.P.H. Chang, using a relatively high-

density plasma (several times  $10^{10} \text{ cm}^{-3}$ ) with short oxidation times (2-5 min), the interface was less than 30 Å for an oxide thickness of 600 Å, and less than 70 Å for a thickness of 2800 Å [19]. For L.A. Chesler and G. Y. Robinson, using a low-density plasma (DC discharge) with long oxidation times (3 to 4 hr) [8], the interface was very wide: about 500 Å. The oxides produced in the multipole are intermediate, which fits in quite well with the oxidation conditions: density of the order of  $10^{10} \text{ cm}^{-3}$  oxidation times distinctly less than those of Chesler and Robinson but greater than those of R.P.H. Chang.

### III.2. - Electrical properties

MOS (metal-oxide-semiconductor) diodes were manufactured by evaporating aluminum through a mask containing holes 80 or 100  $\mu\text{m}$  in diameter.

The breakdown field of the oxides after annealing in nitrogen or nitrogen-hydrogen at 350-400°C was about  $2 \times 10^6 \text{ V/cm}$ . It decreased if the oxide was annealed at temperatures above 450°C, especially if the annealing was done in hydrogen. This special effect of hydrogen is probably due to the formation of crystalline regions of arsenic within the oxide [20].

The capacity-voltage  $C(V)$  and conductance-voltage  $G(V)$  curves of the MOS diodes have been drawn for a 1-MHz measuring frequency using a PAR 410  $C(V)$  curve tracer and between 100 Hz and 100 kHz using a PAR 128 A synchronous detector with the 410 curve tracer.

The results varied with the type of semiconductor oxidized. /16

#### III.2.1. - p-type

Figure 8 shows typical  $C(V)$  and  $G(V)$  curves obtained at 1 MHz for an oxide formed on p-type material ( $7 \times 10^{15} \text{ cm}^{-3}$ ) anneal-

Figure 8. Capacity-voltage curve and conductance-voltage curve (1 MHz)  
for oxide on p-type material ( $7 \times 10^{15} \text{ cm}^{-3}$ )

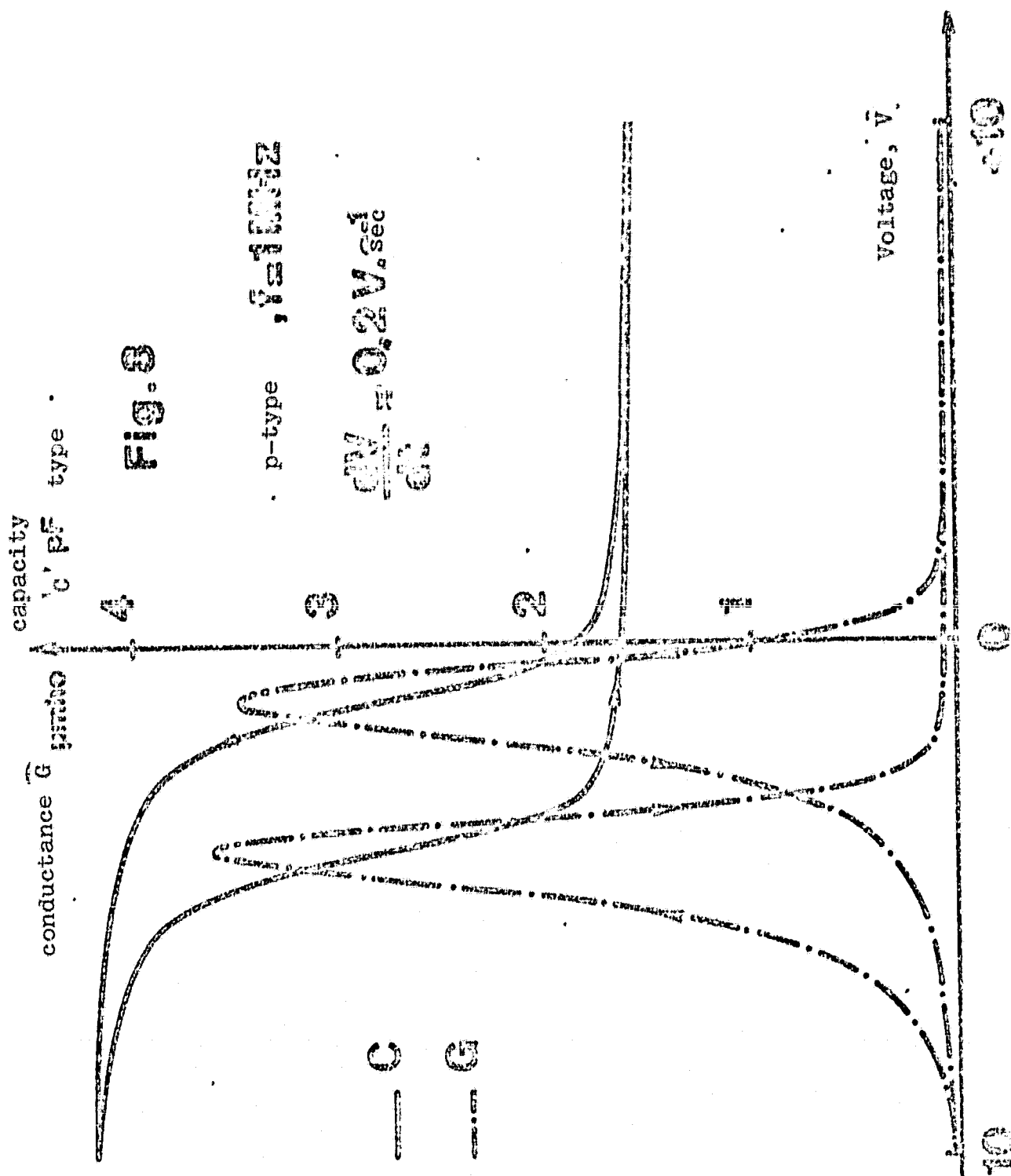
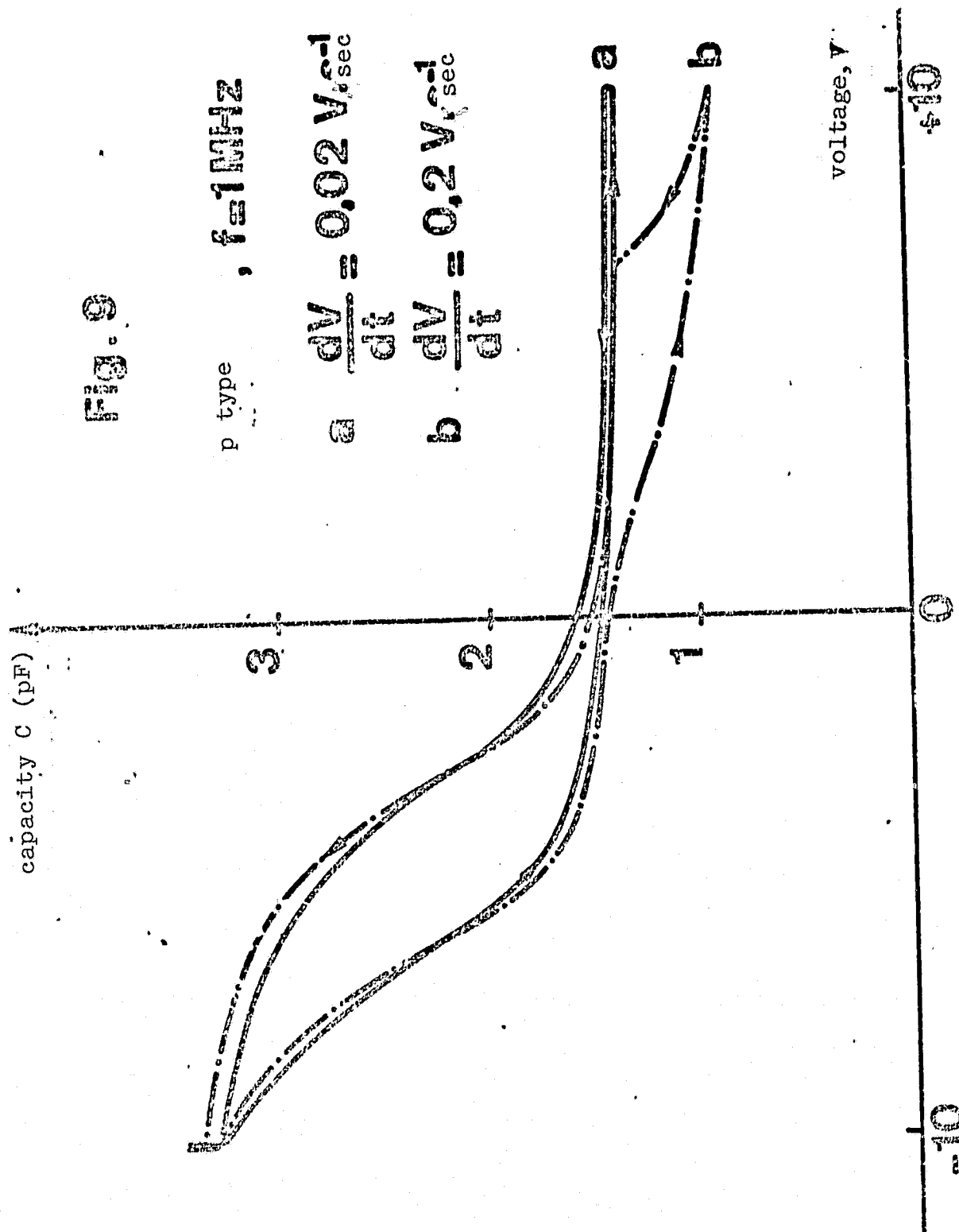


Figure 9. Capacity-voltage curves (1 MHz) of an oxide on p-type material ( $7 \times 10^{15} \text{ cm}^{-3}$ ) at two sweep rates.



ed in nitrogen at 350°C for 30 min. Two very well-defined horizontals of maximum and minimum capacity are seen, together with some counterclockwise hysteresis which increases when the amplitude of the voltage sweep is increased. The sense of this hysteresis shows that it is probably due to capture of holes in the oxide or at the interface when the MOS diode is negatively biased.

If the voltage sweep is faster, an additional hysteresis loop appears in the region of minimum capacity. This can be seen in Figure 9 for the same sample as that of Figure 8, but annealed in nitrogen at 300°C for 30 minutes. The capacity in the maximum shows a "deep depletion" behavior: the sweep is too fast for the capacity to follow it and reach its equilibrium value, represented by the horizontal seen at lower sweep speeds. Comparisons of Figures 8 and 9 also shows that annealing affects this phenomenon: at 0.2 V/sec the deep depletion change is visible in the oxide annealed at 300°C but not in the oxide annealed at 350°C, where it appears only at speeds of the order of 1 V/sec. We have studied the response of the MOS capacity to a voltage step which brings it into the deep-depletion zone. When this step is applied, the capacity goes to a value below the equilibrium value, then tends towards that value more or less rapidly. Physically, the width of the depleted zone exceeds the equilibrium value, then returns to it by recombination of the majority carriers with ionized impurities. Interpretation of the capacity-time curves makes it easy to determine the rate at which electron-hole pairs are generated (Zerbst plot [21]), provided these pairs are created in the depleted zone and not through surface states. If the  $C(t)$  curve has an inflection, volume generation within the depleted zone preponderates in the return to equilibrium; if the curve does not have an inflection, but rather has a concavity pointing downward, surface generation predominates. The latter case is precisely what is observed in our MOS or p-type diodes. Return to equilibrium is thus dominated by processes generating electron-hole pairs to the surface. This took place in about 30 sec for the

/17

sample of Figure 8 when it was subjected to a + 20-V step. A similar observation has been made on an electrochemical anodic oxide [22].

The minimum-capacity horizontal has been interpreted by some writers [1], [8] to be proof that the semiconductor under the oxide can be made to invert. In point of fact, for electrochemical anodic oxide more precise studies of the variation of the surface potential [23], [24] seem to show that inversion is not attained, and that the minimum-capacity horizontal is due to a high density of states at the oxide-semiconductor interface which would trap the Fermi level and limit any extension of the depleted zone and thus of any change in capacity.

We have estimated the density of interface states by Terman's method [25]. This consists of comparing the theoretical  $C(V)$  curve with a  $C(V)$  curve traced at a frequency assumed to be high enough that all the interface states are unable to follow. Under this condition the states are charged or discharged only by the voltage sweep. They behave as if the total charge in the oxide were altered, and displace the  $C(V)$  curve by an amount which varies with  $V$ . The variation of the difference between the theoretical and experimental curves then allows the density of interface states to be calculated. Sources of error in this method are the following:

- a) Even at 1 MHz there can be interface states which follow the signal. In fact, measurements on electrochemical anodic oxide show that the slope of the  $C(V)$  curves decreases above 1 MHz [24], [26].
- b) Drawing the theoretical curve assumes good knowledge of the doping of the semiconductor and precise determination of the capacity of the oxide,  $C_{ox}$ . This is comparable to the maximum capacity measured at low frequency. Examination of the equivalent circuit of a MOS structure (oxide capacity  $C_{ox}$  in series

with a depleted-zone capacity  $C_D$ , the latter in parallel with the conductance  $G_{SS}$  and the capacity  $C_{SS}$  of the interface states which follow the signal) shows that if the measuring frequency decreases, the number of states which can follow it increases, and thus  $C_{SS}$  increases rapidly and makes the capacity tend toward the capacity of the oxide,  $C_{ox}$  [22]. For oxide on the p-type material, we have not observed any significant change in maximum capacity between 100 Hz and 1 MHz. We have taken the value of this maximum capacity to be  $C_{ox}$ .

c) The rate at which the  $C(V)$  curve is scanned must be low enough that slow charge captures and losses in the oxide or at the interface (responsible for the hysteresis) can take place. If the sweep is too fast the slow traps in the oxide and at the interface cannot follow, and are not taken into account in the calculation.

With all these assumptions, one can estimate that the density is around a few times  $10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$  about 0.4 eV above the conduction band. This value is only approximate, however; it is very probably an underestimate. Capacity measurements at frequencies above 1 MHz [24] will soon give a more exact value.

### III.2.2. - n-type

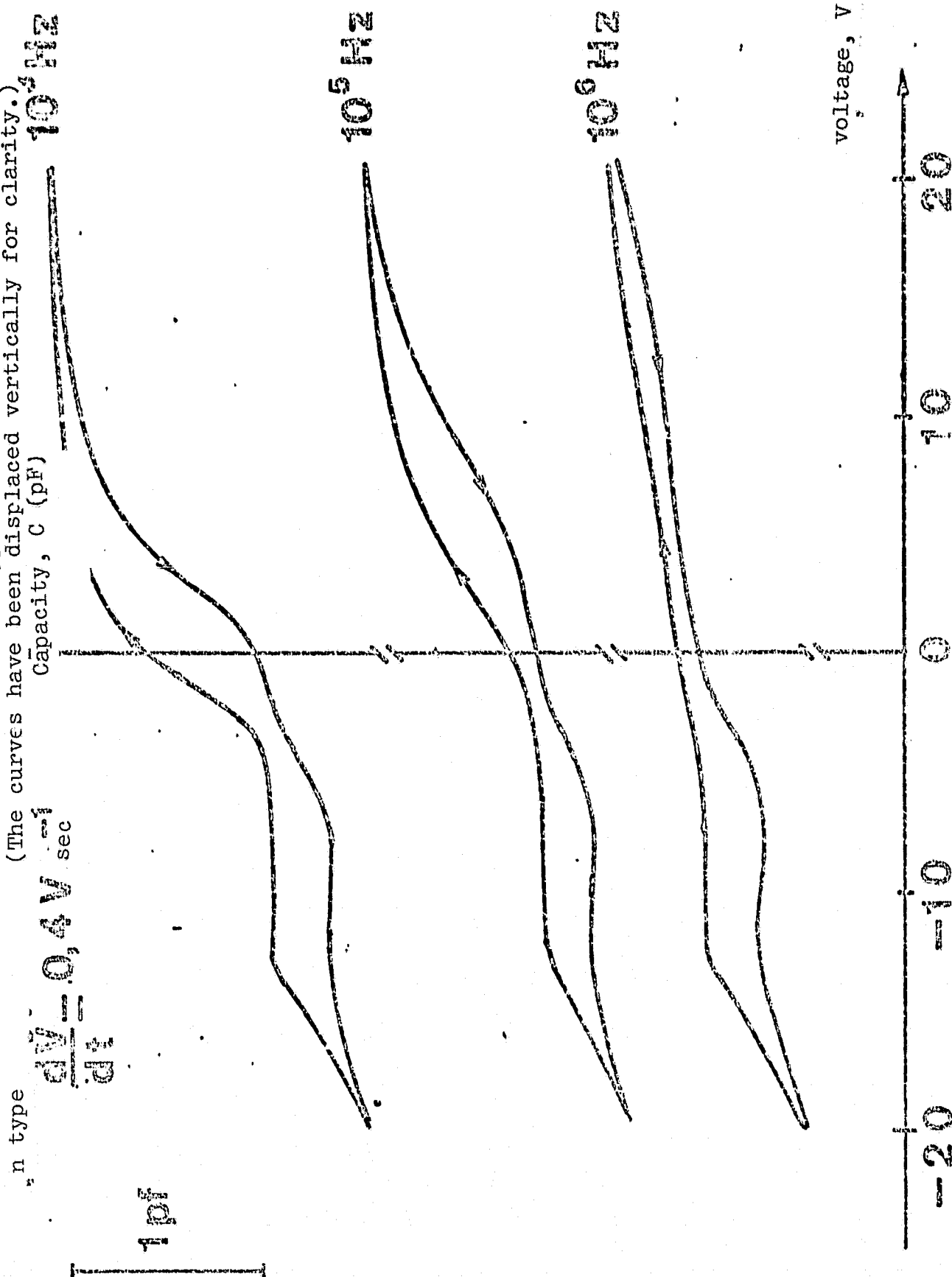
The capacity-voltage curves made on n-type material have a very different appearance from those of the p-type.

Figure 10 shows the  $C(V)$  curves of an MOS diode made on an n-type semiconductor (doped to  $10^{17} \text{ cm}^{-3}$ ) after annealing in nitrogen at 350°C for 30 min.

A certain amount of hysteresis is observed, with its sense opposite to that of the p-type material; this shows the existence of electron trapping and deep-depletion behavior near the /19



Figure 10 Capacity-voltage curves at  $10^6$ ,  $10^5$ , and  $10^3$  Hz of an n type oxide on annealed n-type material 1  
(The curves have been displaced vertically for clarity.)



capacity minimum. The most characteristic feature is the increase in maximum capacity (positive bias) when the frequency of the measuring signal decreases. This frequency dispersion of the capacity has been observed by other authors working with plasma-produced [1], [8] or electrochemical [3] anodic oxide on GaAs.

The shape of the capacity-time curves, when a voltage step is applied which brings the diode into deep depletion, is similar to what is seen for the p-type material. Return to equilibrium is dominated by electron-hole pair generation at the interface.

The frequency dispersion is probably due to a high density of interface states which, when they follow the measuring signal contribute to the total measured capacity and make it tend toward the capacity of the oxide. In fact, if the maximum capacity at low frequency is taken to be the capacity of the oxide, Terman's method can be used to estimate densities of interface states of the order of  $10^{13} \text{ cm}^{-2} \text{ eV}^{-1}$  in the middle of the band gap. This density of states limits the excursion of the Fermi level, which cannot reach the upper half of the gap. The semiconductor under the oxide is always in a depletion state.

The first fabrications of MOSFET transistors on n-type material using electrochemical [3] or plasma [2] anodic oxide showed that in fact such a density of states does not directly limit the ultra-high-frequency properties of these devices. These states are quite incapable of following input-signal changes at the frequencies used (GHz band). On the other hand, the distortions which they introduce into the  $C(V)$  curves can keep an optimum steady-state operating point from being chosen for the device.

A Japanese team at the Fujitsu laboratories has fabricated MOSFET transistors from plasma oxide layers which have comparable capacity-voltage curves [1], [2]. The performance of the device /20

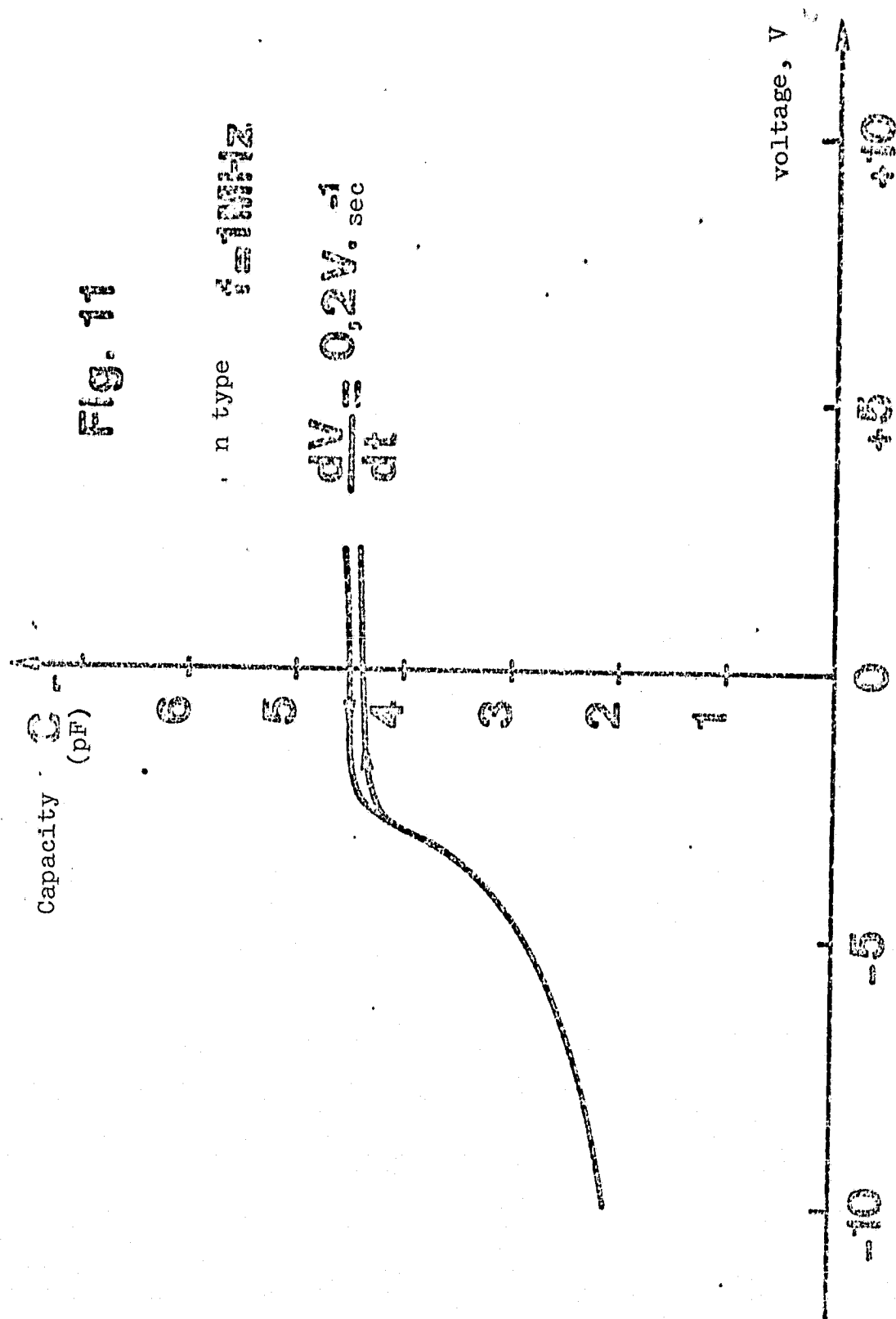
is as follows: 13 GHz maximum enrichment oscillation frequency (positive gate bias), 22 GHz maximum frequency (with a 1.8  $\mu\text{m}$  gate) and 0.4 W output power at 6.5 GHz. To place the performance of the MOSFET transistor in perspective, these authors also built a metal-contact-semiconductor transistor (MESFET) the same size as the MOSFET, using the same technology without the plasma oxidation step. The maximum frequency of this MESFET was 20 GHz, or 10% below that of the depletion MOSFET.

As mentioned above, the annealing atmosphere can play an important role in [determining] the electrical properties of MOS structures. Figure 11 shows a  $C(V)$  curve of an oxide on n-type material ( $4 \times 10^{16} \text{ cm}^{-3}$ ) annealed in hydrogen at  $450^\circ\text{C}$  for 30 min. Compared to the sample annealed in nitrogen, the variation in capacity is clearer even for low sweep rates (40 mV/sec). A similar curve has been published by R.P.H. Chang for plasma oxide produced in the "LAMP" at Bell Labs [5]. This result is a significant improvement over the properties of nitrogen-annealed oxide.

However, annealing in hydrogen degrades the dielectric strength much more than annealing in nitrogen at the same temperature does. For the sample of Figure 10, it was of the order of  $0.5$  to  $1 \times 10^6 \text{ V/cm}$ . Prolonged annealing in hydrogen above  $500^\circ\text{C}$  actually destroys the oxide for all practical purposes [20].

In conclusion, on n-type material the behavior of MOS diodes is controlled by a high density of interface states near the middle of the gap. From the work of Hasegawa and Sawada [23], who studied the electrochemical anodic oxide, it can be expected that this same density also exists on p-type material and explains the minimum capacity horizontal observed in the  $C(V)$  curves. For both types of semiconductor the Fermi level can never reach the upper half of the band gap. Thus, a MOS diode on n-type material could be inversion biased but not accumulation biased, and vice versa for a diode on p-type material.

Figure 11. Capacity-voltage curve (1 MHz) of an oxide on n-type material ( $4 \times 10^{16} \text{ cm}^{-3}$ ) annealed in hydrogen.



### III.2.3. Prospects for improving electrical properties

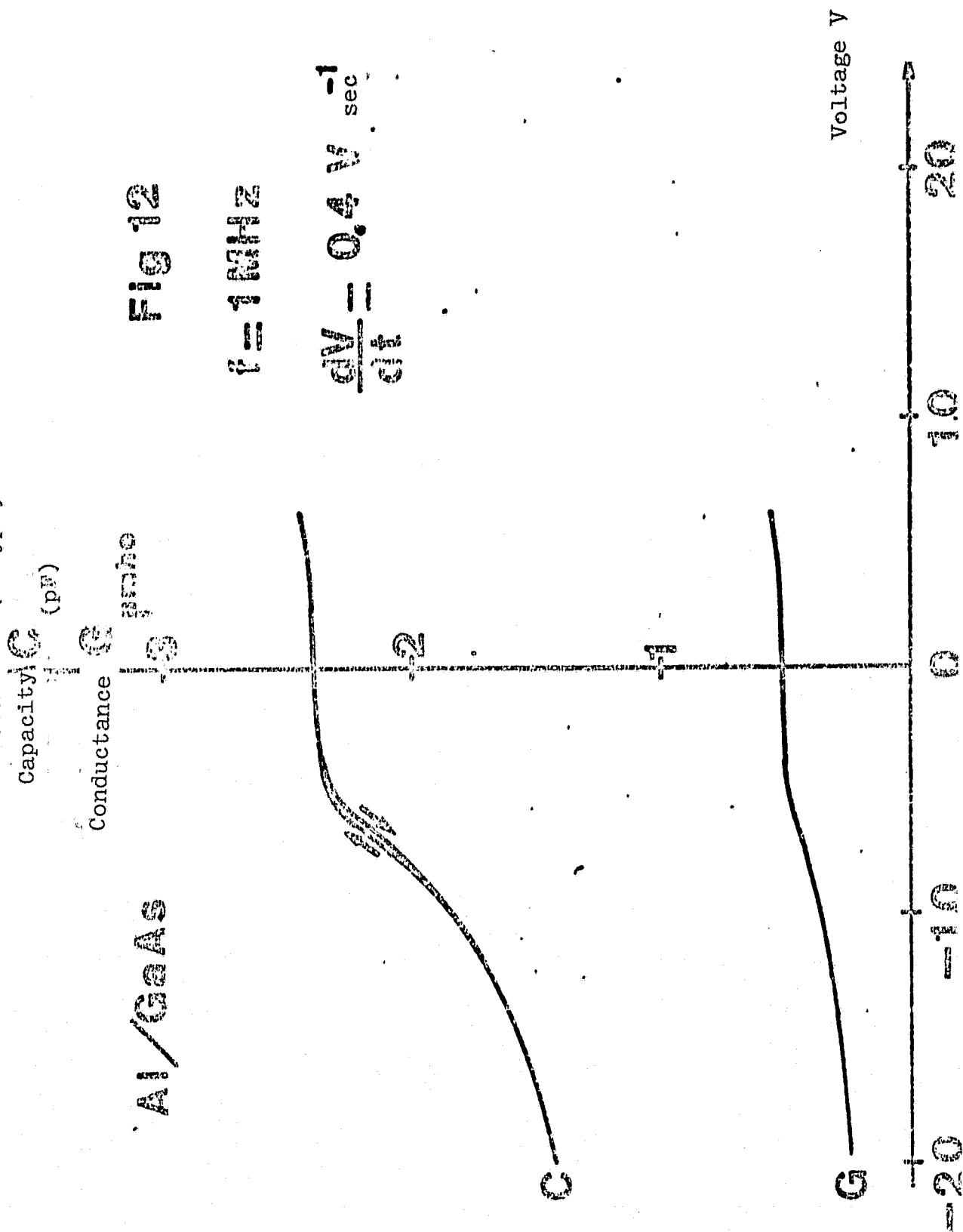
/21

Because of the very different physical and chemical properties of arsenic and gallium, the oxides produced in the multipole, as in other plasma-oxidation devices [8], are arsenic-deficient within the volume and have an arsenic-rich interface. In addition, ellipsometric measurements made at various wavelengths [27] and Auger observations [19] have shown that the oxide and the interface contain an excess of arsenic, partly unoxidized, in proportions which depend on the experimental oxidation conditions. It is possible that differences in arsenic/gallium stoichiometry and the presence of unoxidized arsenic are responsible for the poorer electrical properties of MOS structures on GaAs compared to those on Si. In particular, the high density of interface states deduced from the C(V) curves could be due to the unoxidized arsenic.

Two results published recently seem to confirm these hypotheses: a) - A Japanese team at the Matsushita Electronics Corporation [23] has produced a high-quality thermal oxide (resistivity  $10^{14} \Omega \cdot \text{cm}$ , breakdown field  $5-7 \times 10^6 \text{ V/cm}$ ) by oxidizing GaAs in  $\text{As}_2\text{O}_3$  vapor. Compared to "ordinary" thermal oxides (without external arsenic supply) the stoichiometry is distinctly better. This example shows that the stoichiometry in the volume of the oxide controls the volume properties (breakdown, resistivity) of the layer.

b) Using a thin aluminum film ( $\sim 50 \text{ \AA}$ ) deposited on the surface of the GaAs, R.P.H. Chang at Bell Labs was able to improve the arsenic/gallium stoichiometry of the plasma-produced oxide [17]. During oxidation, the aluminum acts as a filter and limits outward diffusion of arsenic. At the end of oxidation, one finds a layer of GaAs oxide, then a layer of aluminum oxide, then a layer of GaAs oxide. This latter oxide layer is stoichiometric over a good part of its thickness, and especially at the oxide-semiconductor interface, which according to Auger measurements

Figure 12. Capacity-voltage C(V) and conductance-voltage G(V) curves at 1 MHz of an oxidized Al/GaAs structure (n-type,  $4 \times 10^{16} \text{ cm}^{-3}$ )



no longer has an excess of arsenic as GaAs alone does (cf. III.1). After the oxide is annealed in hydrogen at 550°C /22 for 30 min, the properties of the MOS structures obtained seem to be good [6]: breakdown field  $4 \times 10^6$  V/cm, density of interface states in the range of  $10^{10}$  cm<sup>-2</sup> eV<sup>-1</sup> (using the Terman method and the C(V) curve at 1 MHz).

Similar experiments have been performed at LEP with evaporated aluminum films 50 to 100 Å thick. However, the Auger profiles of such a structure after oxidation (Figure 7a) show that arsenic excess is still present at the interface (hatched region). In this case, the aluminum layer did not act as a filter, and did not significantly limit the outward diffusion of arsenic. The electrical properties seem to confirm this observation, since they are not much better than for GaAs alone. Figure 12 shows C(V) and G(V) curves for such a structure (50 Å of Al over n-type GaAs doped to  $4 \times 10^{16}$  cm<sup>-3</sup>) after oxidation and annealing in hydrogen (500 °C, 20 min).

Comparison of this result with those of R.P.H. Chang is an additional indicator that differences in arsenic/gallium stoichiometry in the oxide control the volume properties (resistivity, breakdown field) of the layer, and that the partially unoxidized arsenic excess at the interface is responsible for the high density of states generally observed.

One must thus try to reduce these differences in stoichiometry. Various methods are possible: for example, oxidation or annealing in an arsenic-rich atmosphere, improvement of the filtering properties of a metallic film deposited on the surface of the GaAs, or very fast oxidation in a higher-density plasma to avoid too large a loss of arsenic in the volume and formation of a large excess of partially unoxidized arsenic at the interface. These experiments, combined with more powerful analytical techniques (variable wavelength ellipsometry) might result in improved volume and interface properties of the oxide.

#### IV- Conclusions

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The multipole device is a simple way to obtain an oxygen plasma of good density (a few times  $10^{10} \text{ cm}^{-3}$  with current technology) and good uniformity in a relatively large volume. It is thus perfectly suited to the study of plasma oxidation of GaAs.

In this way, we have been able to produce oxides on GaAs which have usable thicknesses (at least  $1000 \text{ \AA}$ ), typically in 5 min. After annealing in nitrogen, these oxides have electrical properties comparable to the results of other groups working on this subject around the world [1], [5], [8], [10]: breakdown field  $2 \times 10^6 \text{ V/cm}$ ; capacity-voltage curve for p-type material shows a clear maximum and minimum and little frequency dependence (to 1 MHz), for n-type material there is strong frequency dispersion of the capacity maximum, probably due to a high density of interface states ( $\approx 10^{13} \text{ cm}^{-2} \text{ eV}^{-1}$ ) in the center of the band gap. Annealing in hydrogen gives larger capacity modulation, but significantly reduces the breakdown voltage of the oxide.

Comparable results have led to fabrication of depletion and enrichment MOSFET transistors whose electrical properties after improvement could be comparable to those of MESFET transistors (Schottky gate) currently receiving wide attention.

Prospects for improvement are related to reducing the excursions from stoichiometry within the bulk of the oxide and at the interface. In particular, reducing the partially unoxidized arsenic excess at the interface ought to lead to a decrease in the density of states within the band gap, which would allow a larger modulation of the capacity of the MOS structures.



## TECHNICAL APPENDIX 1

/A.T. 1-1

The important parameters of a plasma are the density  $n^+$ , the electron temperature  $T_e$  (giving the thermal energy of the electrons), the plasma potential  $V_p$ , and the relative electron density  $\beta$  (the ratio of electron density to plasma density).

This appendix describes the practical method used in this work to determine  $n^+$  and  $\beta$ .

For a thin cylindrical probe (diameter  $d$ , length  $l$ , with  $d \ll l$ ) immersed in a plasma and biased by a voltage  $V$  with respect to  $V_p$ , it can be shown in [a] that the current  $I_+$  due to ions of mass  $m_+$  (assumed to be singly ionized) and density  $n_+$  is:

$$I_+ = n_+ \cdot \pi \cdot d \cdot l \cdot \sqrt{\frac{2eV}{m_+}} \quad (e = \text{the electron charge}).$$

In particular, for negative biases, only positive ions of mass  $m^+$  will be attracted; their density  $n^+$  is the plasma density:

$$n^+ = \sqrt{\frac{2eV}{m_+}} \cdot \frac{1}{\pi d l} \cdot \frac{I_+}{\sqrt{-V}}$$

$V_p$  is small, of the order of a few volts from ground. If the probe is biased to a few tens of volts,  $V$  can be taken to be the bias voltage of the probe from ground, and  $V_p$  can be neglected. If  $m^+$  is known,  $n^+$  can then be calculated by measuring  $I_+$ . In our study, inspired by similar experiments [b], we took  $O_2^+$  to be the positive ion.

The relative electron density  $\beta$  was calculated by comparing the currents in the probe for biases  $v_{\pm}$  on both sides of  $V_p$  which were large compared to  $V_p$  [c] and to the thermal energies of the components of the plasma. (In practice, it is sufficient

to take V to be a few tens of volts).

For a thin probe, it can be shown that:

$$\beta = \frac{R \sqrt{\frac{m^+}{m^-}}}{\sqrt{\frac{m^+}{m_e}} - \sqrt{\frac{m^+}{m^-}}} \quad \text{A.T.1-2}$$

where R is the ratio of the probe current for V positive to the current for V negative;

$m^-$  is the mass of the negative ion (only one assumed);

$m_e$  is the electron mass.

In our study we have assumed that the negative ion is  $\text{NO}_2^-$  [b].

[a] See, for example

J. Virmont, Doctorat es-Sciences-thesis - Ecole Polytechnique - 1969)

[b] M. Bacal, H. J. Doucet, Vacuum 24, 595 (1974).

[c] H. J. Doucet, Phys. Let. 33A 283 (1970).

Method of calibrating analyses by Auger spectrometry

The Auger signal can be converted into concentration by the sensitivity-factor method described by C.C. Chang [a].

$$H_i = \alpha_i h_i / \sum_y \alpha_y h_y$$

In this expression,  $H_i$  is the concentration of element  $i$ ,  $h_i$  is the Auger signal of element  $i$  determined by the peak-to-peak height in the spectrum of  $\frac{dN(E)/dE}{dE}$  as a function of  $E$ , and  $\alpha_i$  is the inverse of the sensitivity factor for element  $i$ .

This type of formalism does not take account of the matrix effects: change of shape and energy of the Auger peaks, electron backscattering, diffraction of primary electrons, etc.

This difficulty can be avoided by using standards to determine a new sensitivity factor for each matrix. This is the approach which was chosen for the study of GaAs oxides.

In this calibration method it is not necessary to determine the  $\alpha_i$  absolutely, and consequently gallium was chosen as the reference element.

a) - Determination of the  $\alpha_i$  coefficients for gallium arsenide

The sensitivity factors were determined on (001) surfaces of GaAs for the following cases: after ion cleaning, after molecular-beam growth, after cleaning the surface by thermal treatment in ultra-high vacuum [b].

$$\begin{aligned} \alpha_{Ga} &= 1 \\ \alpha_{As} &= 1.7 \quad (*) \end{aligned}$$

b) - Determination of the  $\alpha'_i$  coefficients for GaAs oxide. /A.T.2-2

The sensitivity factors were determined on pressed-powder specimens. As C. C. Chang did [c], we observed a change in the amount of arsenic at the specimen surface which was produced by the electron beam and caused us to make a correction to the sensitivity factor for arsenic. In contrast, the sensitivity factor for oxygen as measured on  $\text{Ga}_2\text{O}_3$  specimens did not change significantly during ion or electron bombardment.

$$\alpha'_{\text{Ga}} = 1$$

$$\alpha'_o = 0,67$$

$$\alpha'_{\text{As}} = 2,61 (*)$$

c) The sensitivity coefficient of aluminum in the oxide was measured by using a corundum specimen as the reference.

$$\alpha'_{\text{Al}} = 1,54$$

(\*) These inverse sensitivity factors are applicable only to measurements made under the following conditions:

- peak-to-peak modulation: 5V
- analyzer resolution: 0.3%
- incident electron energy: 2.5 keV
- incident electron flux:  $8 \times 10^{17} \text{ e/cm}^2 \text{ sec}^{-1}$ .

- [a] C. C. Chang, Characterization of Solid Surfaces (P. F. Kane and G. B. Lattabel, Plenum Press, New York, 1974) pp. 509-575.
- [b] G. Laurence, F. Simondet and P. Sajet accepted for publication in Applied Physics.
- [c] C. C. Chang, R.P.H. Chang and S.P. Murarka, J. Electrochem, 125, 481 (19 ).

## TECHNICAL APPENDIX 3

July 1978

### USE OF MULTIPOLE PLASMA FOR THE OXIDATION OF SEMICONDUCTORS

by

S. Gourrier, A. Mircea  
Laboratoire d'Electronique et de Physique Appliquée  
94450 Limeil-Brevannes, 3 avenue Descartes (France)

and

M. Bacal  
Ecole Polytechnique  
91128 Palaiseau Cedex (France)

#### 1. Introduction

In the last few years there has been an increasing interest in GaAs plasma oxidation [1-4]. This interest is related to the potential use of this semiconductor in M.O.S. (Metal-Oxide-Semiconductor) devices. The oxide layer should meet the following requirements :

- a high resistivity (at least  $10^{12}$ - $10^{13} \Omega \cdot \text{cm}$ ) ;
- a high enough breakdown voltage to allow biases up to 20-30 V (breakdown fields higher than  $2\text{-}3 \cdot 10^6$  V/cm for a typical oxide thickness of 1000 Å) ;
- a density of interface states and fixed bulk charges lower than  $10^{11} \text{ cm}^{-2}$ .

Using a large capacity multipurpose plasma reactor (LAMP), Chang and Sinha [1] have obtained promising results in oxidizing GaAs in a magnetically confined oxygen plasma produced by a RF discharge. The successful operation of a depletion MOSFET with plasma oxidized GaAs has also been reported [4]. However, the equipment previously used for plasma oxidation was generally sophisticated and costly.

We proposed and tested an oxygen multipole type plasma [5] for studying the plasma oxidation of GaAs and other semiconductors. We found that this cheap and efficient plasma source is adequate for the oxidation of GaAs surfaces.

This paper presents the structure and characteristics of the multipole plasma source as well as some preliminary results concerning the electrical and physical properties of the oxides prepared in this source.

## 2. The multipole oxygen plasma

A few years ago Limpacher and MacKenzie [5] reported the use of a multipole type device for producing large, homogeneous and quiescent argon plasma. The multipole device consists of a plasma source located inside a "magnetic" plasma container (Figure 1). The plasma source consists of one or several electron emitters (e.g. hot tungsten filaments), biased negatively with respect to the walls of the magnetic plasma container; the primary electrons ionize the low pressure gas admitted in the vessel.

The plasma container is a magnetic structure made of small permanent magnets presenting alternatively their south and north poles towards the plasma. The permanent magnets can be fixed outside the vacuum chamber in which the plasma is produced. The magnetic field created at the plasma surface can reflect the ionizing primary electrons as well as the plasma electrons and ions. For a given neutral density and electron emission current, the use of the magnetic plasma container leads to an increase in plasma density of two or three orders of magnitude.

Recently, the multipole device has been used in fields other than the fundamental research in plasma physics for which it had been originally destined. Thus the use of the multipole configuration for the production of intense positive and negative hydrogen ion beams has been recently reported [6,7]. The properties of the multipole plasma (homogeneity, large volume, high degree of gas ionization) seems highly suitable for application in plasma chemistry; however, to the best of our knowledge, the use of a multipole device has not yet been described for this application.

It has been demonstrated [8] that a "diffusion-type" oxygen plasma of  $\sim 10^9 \text{ cm}^{-3}$  could be produced at vacuum levels ranging from  $10^{-3}$  to  $10^{-4}$  Torr, using Tungsten or Rhodium electron emitters. The multipole confinement can increase the possible lifetime of the electron emitters; an oxygen plasma density of  $10^{10} - 10^{11} \text{ cm}^{-3}$  is produced using modest electrical power at an oxygen pressure of  $10^{-4} - 10^{-3}$  Torr.

Our multipole system is shown on Fig.1. It consists mainly of a non-magnetic stainless-steel cylinder around which columns of permanent magnets are mounted. The magnetic confinement on top and bottom of the multipole is achieved by two discs which also support stacks of permanent magnets and are located inside the vacuum chamber. The electron source is a tungsten filament of 0,3 mm diameter. Under typical operating conditions, its lifetime is about 15 hours.

Figure 2 shows the variation of plasma density versus discharge current and discharge power (the heating power dissipated in the filament is not included), as obtained in the above described multipole.

The plasma density is determined from the ionic branch of the characteristic of a thin cylindrical electrostatic probe. This characteristic also gives the relative electron density in the plasma [9] :

$$\beta = n_e/n_+$$

Figure 3 shows the measured variation of the relative electron density versus the plasma density.

The mass analysis of the ion species present in the multipole plasma was not effectuated. However, the analysis of the negative ion species present in the diffusion type oxygen plasma [8] has shown that the dominant negative ion species was dependent on the nature of the used electron emitter. When a Tungsten filament is used, the dominant negative ion was the impurity ion  $\text{NO}_2^-$ ;  $\text{O}^-$ ,  $\text{O}_2^-$  and  $\text{NO}_3^-$  ions are also present. When a Rhenium emitter is used, the dominant negative ion is  $\text{O}_3^-$ .

### 3. GaAs plasma oxidation

The first sample holders that were used did not allow the control of the temperature of the samples during the oxidation, which under typical operating conditions could reach 150°C-200°C. Since the heating of the sample during plasma oxidation may be a serious problem (it may affect the density and the stoichiometry of the oxides) a sample holder, was designed which can be cooled by water or liquid nitrogen.

In this device, the sample is placed on a small copper disc mounted on a copper pedestal in which water or liquid nitrogen can flow. This disc is electrically isolated by a thin mica sheet, whilst maintaining a good thermal contact with the pedestal. The sample edges are covered by an alumina cap. In this way, any distortion of the electrical field which could be due to irregular edges and which could lead to oxidation inhomogeneities can be avoided. Furthermore, with this geometry the sample surface acts as the only anode surface within the multipole volume. A small tantalum plate has been mounted under the filament to avoid direct contamination of the sample.

Oxidations have been carried out mostly on n-type ( $2 \times 10^{18} \text{ cm}^{-3}$ ) and sometimes on p-type ( $7 \times 10^{15} \text{ cm}^{-3}$ ) [100] GaAs. Before being oxidized, the wafers were degreased, deoxidized in boiling hydrochloric acid and thoroughly rinsed in deionised water. More elaborate surface preparation techniques are presently under study in our laboratory and will soon be employed in this work.

The whole system is pumped down to about  $10^{-6}$  Torr and then filled with oxygen (99.998%). Under typical oxidation conditions, the oxygen pressure is about  $8 \times 10^{-4}$  Torr, the emission current ranges from 20 to 100 mA (corresponding to plasma densities from  $5 \times 10^9 \text{ cm}^{-3}$  to  $2 \times 10^{10} \text{ cm}^{-3}$ ). The sample voltage is a few tens of volts positive with respect to the plasma, and the current density on the sample surface is 1 to 7 mA/cm<sup>2</sup>. If this density is held constant, the variation of the sample voltage can be monitored: after an initial (5-10 nm) rapid rise (2-3 V/nm with a current density of 5-7 mA/cm<sup>2</sup>), a slower rate is observed. The ratio between the voltage variation and the final oxide thickness is about 40 Å/V, a value similar to that of other authors working on GaAs plasma oxidation [1,3] and which is two times higher than in the case of anodic oxidation. Using this technique, homogeneous oxides with thicknesses in the range 1000-2000 Å can be obtained in 20-30 nm. The maximum temperature during the oxidation is about 80-90°C with water cooling.

#### 4. Properties of the oxide layers

The oxide layers have been analyzed using Auger spectroscopy and SIMS. The Auger calibration method is analogous to that of Chang et al. [10] and yields approximately the same correction factors. For previous oxides made without any cooling, an almost constant depth profile is obtained with typical concentrations of O = 50%, Ga = 35%, As = 15%. The first Auger results concerning oxides made at lower temperatures ( $T_{\text{max}} = 90^\circ\text{C}$ ) give approximately the same values but with a slight decrease of the oxygen concentration (55% at the surface, 50% at the interface) and a corresponding increase of the arsenic concentration (10% at the surface, 15% at the interface) while the gallium concentration remains about 35%. For both types of samples, the interface transition was estimated to be 150-200 Å. No pollution could be detected either by Auger or by SIMS analysis.



Ellipsometric measurements at 6328 Å gave a refractive index of 1.85-1.9.

M.O.S. diodes were fabricated by evaporating aluminium through a mask with apertures of 80  $\mu\text{m}$  diameter. The dielectric breakdown field of the oxide is about  $2 \times 10^6$  V/cm. C(V) curves of annealed n and p type samples are shown in figures 4, 5 and 6. They show some characteristic features already mentioned by other workers for plasma [2,3] or anodic [11] oxides. For n type samples (Fig. 4) a clockwise hysteresis and a frequency dispersion in the so-called accumulation region can be seen. This latter phenomenon can be interpreted, as stated by other workers [11] by the presence of a high density (in the  $10^{13}\text{cm}^{-2}\text{eV}^{-1}$  range) of interface states near the conduction band preventing the sample to be biased into accumulation. For p type samples (Fig. 5), a well defined minimum capacitance and some hysteresis are observed. Increasing the sweep rate tends to create a loop in the minimum capacitance region but does not change the amplitude of the hysteresis (Fig. 6). No noticeable frequency dispersion of the maximum and minimum capacitances values could be seen from 100 Hz to 1 MHz. For both types of samples, the effectiveness of the annealing treatment, e.g. 30 min at 350°C in nitrogen, was clearly demonstrated, especially in reducing the hysteresis amplitude.

In conclusion, the multipole principle has provided a simple and convenient plasma source allowing the study of plasma grown oxides on GaAs. Further studies are presently being performed in order to improve the electrical properties of the oxides and to obtain a better knowledge of the oxide-semiconductor interface.

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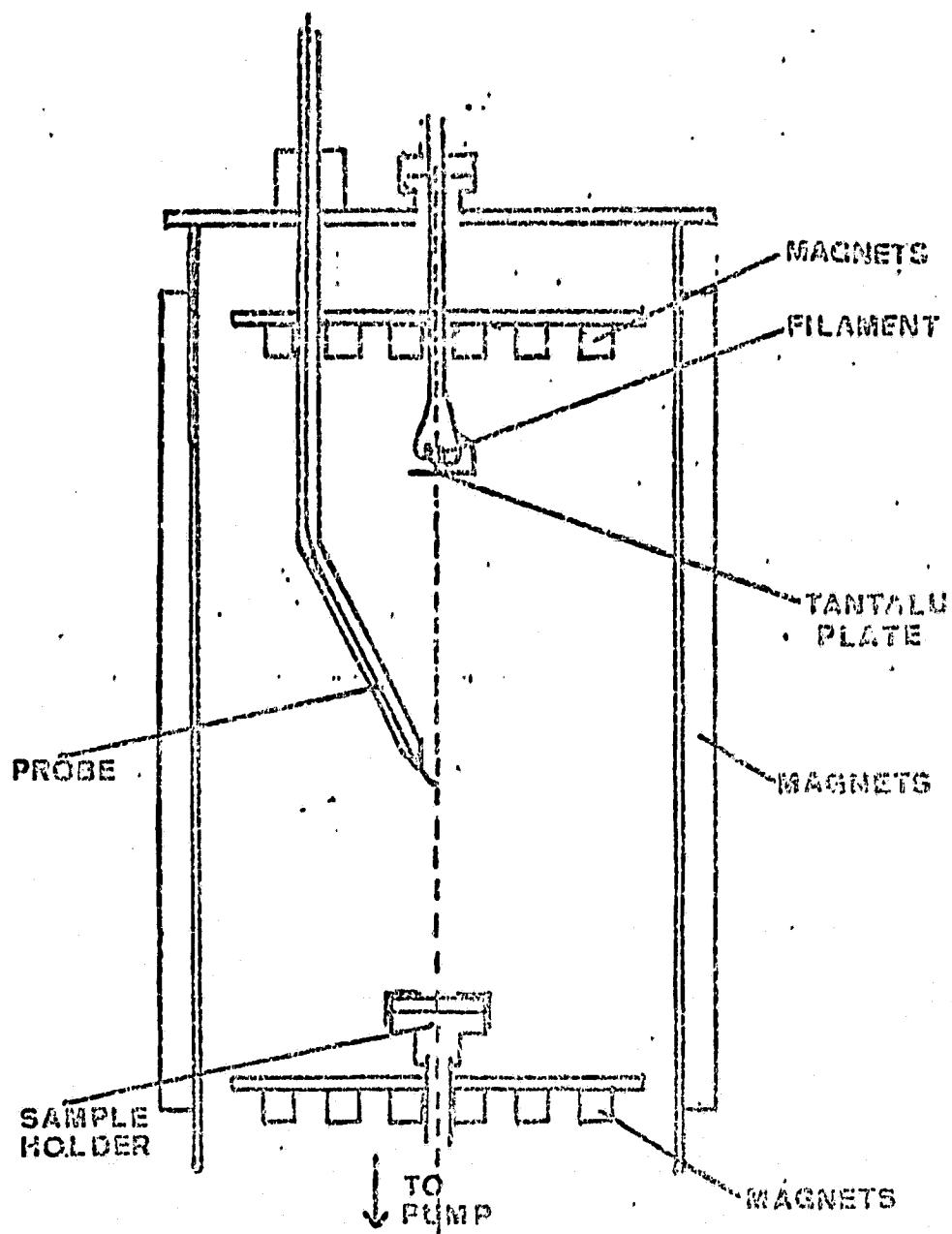


Figure 1: Schematic of the multipole chamber

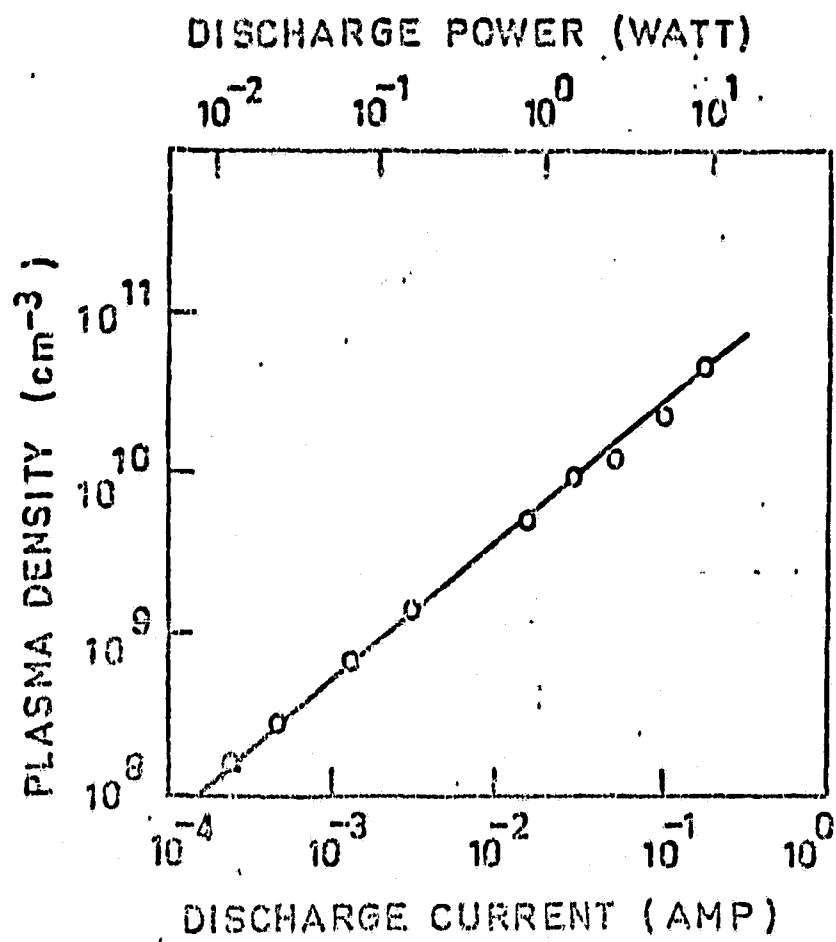


Figure 2: Plasma density measured on our multipole versus discharge current and discharge power.

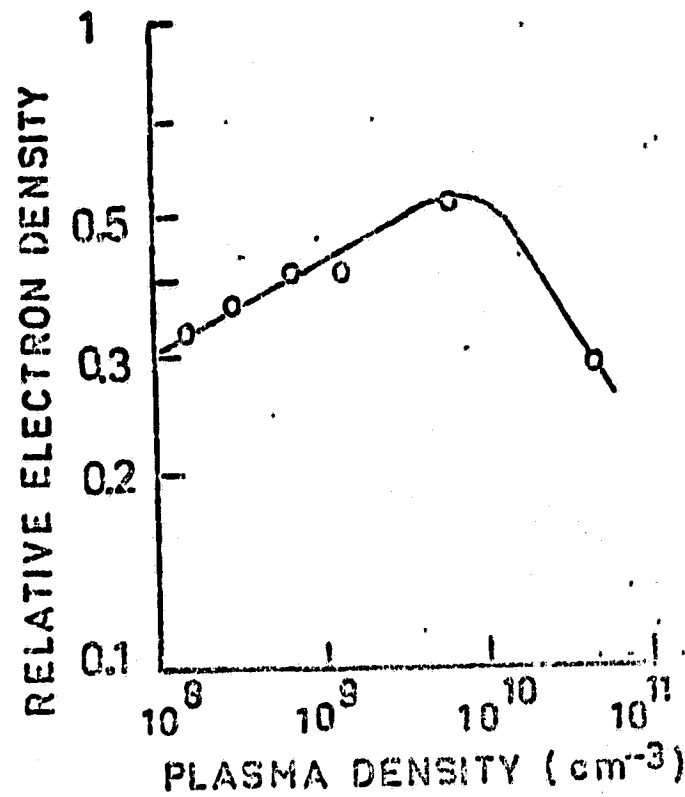


Figure 3: Relative electron density  $\beta = n_e/n_+$  versus plasma density.

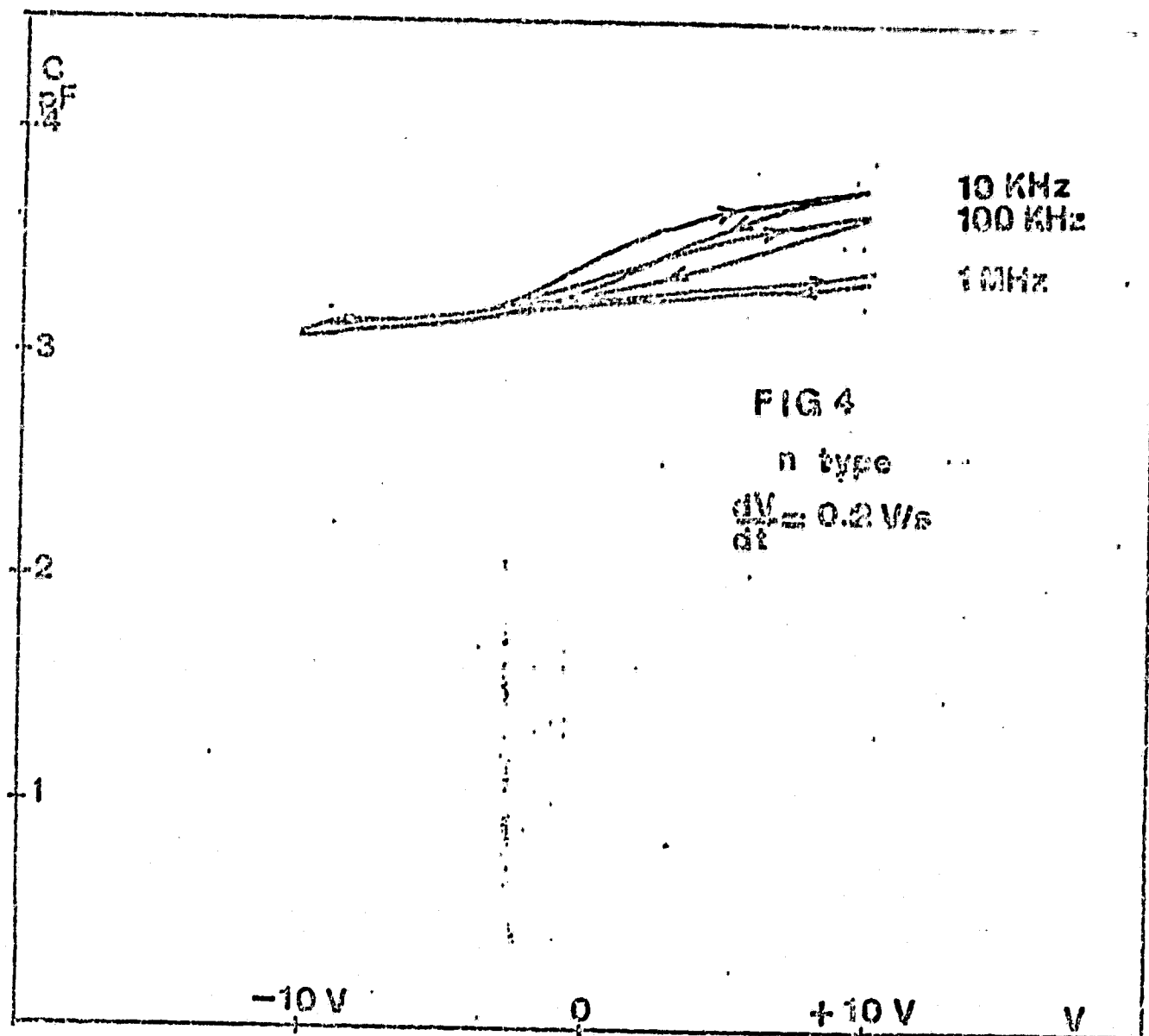


Figure 4: C(V) curves of a n type ( $2 \times 10^{18} \text{ cm}^{-3}$ ) sample showing frequency dispersion.

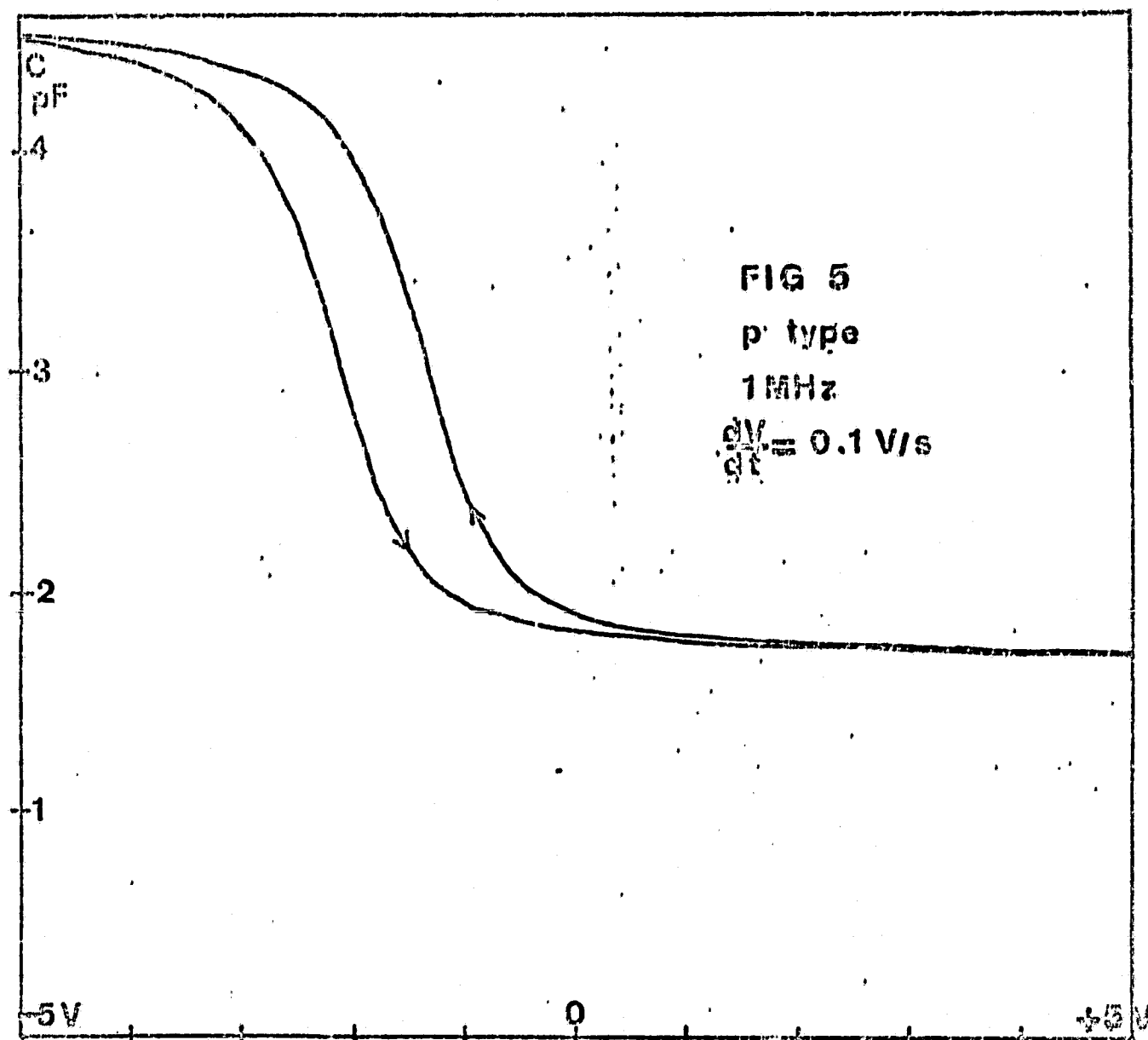
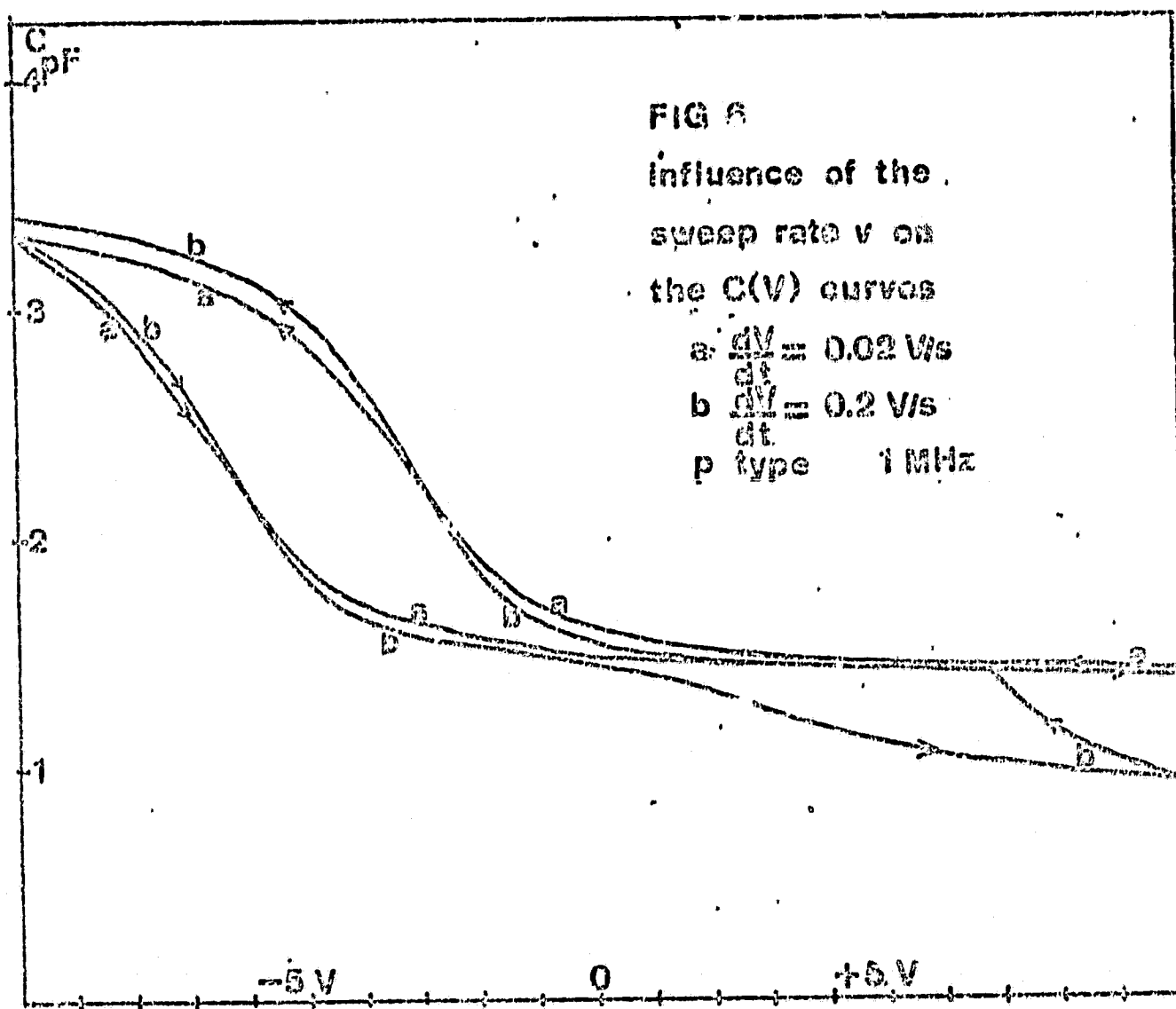


Figure 5:  $C(V)$  curve of a p type ( $7 \times 10^{15} \text{ cm}^{-3}$ )



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Figure 6:  $C(V)$  curve of a p type sample showing  
the influence of the sweep-rate  $\frac{dV}{dt}$



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The GaAs layers to be oxidized were prepared at LEP by vapor-phase epitaxy on highly doped substrates by Madam Mennechez of M. Hollan's department.

S. Gourrier and A. Mircea carried out the oxidations of the samples and the study and interpretation of the MOS structures obtained.

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